Sampling and Analysis for the Lake Tahoe Atmospheric Deposition Study

Final Report

Appendix A: Standard Operating Procedures for Laboratory Operations

Presented to:

Research Division, California Air Resources Board
1001 I Street
Sacramento, CA 95814

June 1, 2005

Table of Contents

APPENDIX A.1 ..... A-1

APPENDIX A.2 ..... A-13

APPENDIX A.3 ..... A-54

APPENDIX A.4 ..... A-82

APPENDIX A.5 ..... A-197

APPENDIX A.6 ..... A-260

APPENDIX A.7 ..... A-277

APPENDIX A.8 ..... A-315

APPENDIX A.9 ..... A-350

APPENDIX A.1

DRI STANDARD OPERATING PROCEDURE

Pages: 397
Date: 4th Quarter 1994

Title: Impregnating, Drying, and Acceptance Testing of Filters for Sampling Gases in Air

Number: 2-104.3
Revision: 3

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This standard operating procedure describes the inspection, impregnation, vacuum drying, storage, and acceptance testing of filters impregnated with citric acid, potassium carbonate (K_2CO_3), and triethanolamine (TEA) for collecting ammonia (NH_3), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2), respectively. This procedure will be followed by all analysts at the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute (DRI).

1.2 Measurement Principle

A selected filter substrate is impregnated with gas-absorbing solution to collect gaseous species existing in the atmosphere. The impregnation solutions differ with respect to their reactive components and with respect to their formulations. The following criteria must be met by the impregnation solutions:

- Purity of reagent.
- Stability of the impregnation solution composition before and after impregnation.
- Low degree of hazard or toxicity.
- Lack of interferences with other pollutants being sampled or with analytical methods.
- Minimal effects of environmental factors such as temperature and water vapor content.

The impregnation solutions listed below were developed based on these criteria and extensive laboratory tests.

- 15% K_2CO_3 and 5% glycerol solution (balance being DDW) for SO_2 sampling.
- 25% citric acid and 5% glycerol (balance being DDW) for NH_3 sampling.
- 25% triethanolamine, 4% ethylene glycol, (balance being DDW) for NO_2 sampling.

1.3 Measurement Interferences and Their Minimization

All filters are used for collecting minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters during the inspection and impregnation procedures. Special precautions include the following:

- Never handle a filter with anything other than clean flat-tipped tweezers.
- Handle the filters only on the edges. Touching the tweezers to the central portion can damage a filter.
- Human breath contains ammonia. Therefore, avoid breathing on any filters; particularly the citric acid-impregnated filters, since they will collect ammonia from human breath.
- Impregnating procedures should be carried out under the laminar flow-hood or in a clean room with HEPA filter filtration.

1.4 Ranges and Typical Values of Measurements

Concentrations of gases collected by impregnated filters are highly specific as to species as well as location and time. Concentrations for collected gases are generally in the range of 0.01 to 500 $\mu g/m^3$.

Concentrations of certain ions on the impregnated, unsampled filter substrates must fall within acceptabel limits for the filters to be useful for sampling. The acceptance test criteria are listed in section 6.2.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

Not applicable.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing filter impregnation, which includes solution preparation, filter impregnation, assigning of blanks, and acceptance testing of filters.

It is the responsibility of the laboratory manager or supervisor to insure the impregnation procedures are properly followed, to verify that filter blanks have been assigned, to maintain the supplies necessary to insure uninterrupted impregnation, and to oversee proper chain-of-custody documentation.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

(Not Applicable)

1.8 Related Procedures

- DRI SOP # 2-203.4 Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography (IC)

- DRI SOP # 2-207.3 Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetry (AC)
- DRI SOP # 2-206.2 Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy (AAS).

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus

- Sartorius R160D Analytical Balance
- Teflon impregnation container with lid. (Savillex, Minnetonka, MN)
- Sonicator: Branson Model 5200 (Fisher Scientific, Santa Clara, CA)
- GLAS-COL Shaker #14-258 with Test Tube Rack holder #14-259-3 (Fisher Scientific Co., Santa Clara, CA)
- Light Table
- Vacuum Oven, Model 1410 (VWR Scientific Co., Santa Clara, CA)
- 5 cm Hirsch funnel and vacuum flask (500 ml)
- Flat-tipped tweezers. (Millipore, San Francisco, CA)
- 500 ml volumetric flask for each solution to be prepared
- 500 ml glass or plastic bottles with screw tops for storage of impregnating solutions. (CAUTION: TEA SOLUTION SHOULD BE STORED IN AN AMBER BOTTLE.)
- Spatula
- Plastic weighing boats
- Parafilm
- PVC gloves, non-powdered

2.2 Reagents

All chemicals should be ACS reagent grade.

- Citric acid monohydrate, granular.
- Potassium carbonate, anhydrous.

- Triethanolamine, Baker Analyzed Reagent (J.T. Baker, Inc., Phillipsburg, NJ)
- Glycerol, Anhydrous, Baker Analyzed Reagent (J.T. Baker, Inc., Phillipsburg, NJ)
- Ethylene glycol, Baker Analyzed Reagent (J.T. Baker, Inc., Phillipsburg, NJ)
- Methanol, Absolute, Acetone free

2.3 Filter Supplies

- Pallflex 2500 QAT-UP quartz-fiber filters, 47mm or 25mm for K_2CO_3 impregnation. (PALLFLEX Products Corp., Putnam, CT)
- Whatman 41, cellulose-fiber filters, 47mm for citric acid or K_2CO_3 impregnation. (CHEMTREX, Hillsboro, OR)
- Whatman 31ET chromatography paper, 47mm for TEA impregnation. (CHEMTREX, Hillsboro, OR)

2.4 Filter Batch Labels

The impregnated filters are prepared in batches of one hundred. The containers for these batches are labeled with DRI assigned lot numbers. The filters are assigned sequential lot numbers, in lots of 100, when received from the supplier. The last lot number used can be determined from the Filter Acceptance Log Sheet (Figure 2-1).

2.5 Forms

Filter Impregnation Log Sheet (Figure 2-1).

3.0 CALIBRATION STANDARDS

Not Applicable.

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram for this procedure is shown in Figure 4-1.

4.2 Preparation of Impregnating Solutions

4.2.1 Potassium Carbonate Impregnation Solution (15% K_2CO_3, 5% Glycerol, and 80% DDW)

- Using an analytical balance, weigh 100 g of potassium carbonate, anhydrous, (K_2CO_3**)** into a weighing boat. Transfer quantitatively into a 500 ml volumetric flask.

- Add about 200 ml distilled-deionized water (DDW) to dissolve crystals. Sonicate until completely dissolved.

Figure 2-1. Log Sheet for Filter Impregnation

Figure 4-1. Flow Diagram of Filter Impregnation Procedure.

- Weight 25 g of glycerol into a weighing boat**,** and add to the solution in the volumetric. Rinse boat well with DDW, adding this rinse water to flask. Add DDW to the 500 ml mark and mix well.

- Obtain a 500 ml plastic bottle with a tight fitting screw lid. Rinse bottle at least three times with DDW prior to solution transfer.

- Label bottle clearly with the contents, date of preparation, and the initials of the preparer. Transfer the K_2CO_3 solution to the bottle.

4.2.2 Citric Acid Impregnation Solution (25% citric acid, 5% Glycerol, and 70% DDW)

- Using an analytical balance, weigh 125 g of citric acid monohydrate into a weighing boat. Transfer quantitatively into a 500 ml volumetric flask.

- Add about 200 ml DDW to dissolve crystals and sonicate until completely dissolved.

- Weigh 25 g of glycerol and add to the citric acid solution. Add DDW to bring to the 500 ml mark and mix well.

- Obtain a 500 ml plastic bottle with a tight-fitting screw lid. Rinse bottle at least three times with DDW prior to solution transfer.

- Label bottle clearly with the contents, date of preparation, and the initials of the preparer. Apply an appropriate barcode label. Transfer the citric acid solution to the bottle.

4.2.3 TEA Impregnation Solution (25% Triethanolamine, 4% Ethylene glycol, 25% Methanol, and 46 % DDW)

- Using an analytical balance, weigh 125 g of triethanolamine into a weighing boat.

- Transfer quantitatively into a 500 ml volumetric flask.

- Add 125 ml of methanol to the flask.

- Weigh 20 g of ethylene glycol and add to flask. Bring up to the 500 ml volume mark with DDW and sonicate until solution is clear.

- Obtain a 500 ml amber plastic bottle with a tight-fitting screw lid. Rinse bottle at least three times with DDW prior to solution transfer. (CAUTION: TEA SOLUTION MUST BE STORED IN AN AMBER PLASTIC BOTTLE.)

- Label bottle clearly with the contents, date of preparation, and the initials of the preparer. Transfer the TEA solution to the bottle.

4.3 Inspection and Impregnation of Potassium Carbonate Filters

4.3.1 Open one box of 47 mm Whatman 41 filters or four boxes of 47 mm Pallflex 2500 QAT-UP or one box of 25mm Pallflex quartz-fiber filters. (Whatman 47 mm and Pallflex 25 mm filters are 100 filters/box, Pallflex 47 mm filters are 25 filters/box.)

4.3.2 Assign DRI batch ID and place filters in the Teflon impregnation jar. Approximately 100 filters can be impregnated in this container.

4.3.3 Add approximately 100 ml of the impregnation solution, making sure there is enough solution to totally submerge the filters. Place the lid on the container and tightly seal.

4.3.4 Clamp the container to the test tube shaker and immobilize the impregnation container in the shaker using a piece of foam rubber and clamp bar. Agitate slowly by adjusting the speed to 60 cycles per minute (knob setting at 3) and leave it on for 30 minutes.

4.3.5 Remove the impregnation container from the shaker and decant the impregnation solution. Transfer the stack of filters to a five cm Hirsch funnel and place a sheet of parafilm on the top of the funnel.

4.3.6 Place the funnel into a 500 ml vacuum flask and apply a vacuum by connecting a vacuum hose from the flask sidearm to the house vacuum connection and turning valve. Allow the vacuum to draw off all of the excess wash solution from the stack of filters. The parafilm will be drawn into the funnel and will press over the filter stack to press out excess liquid. When the solution is dripping at a rate of 2 drops/sec., transfer the stack of filters back to the impregnation container and continue with Drying Procedure in Section 4.6

4.4 Inspection and Impregnation of Citric Acid Filters

4.4.1 Open a box of 100 47 mm Whatman 41 filters.

4.4.2 Place the filters in the Teflon impregnating container.

4.4.3 Add approximately 100 ml of the citric acid impregnation solution, making sure that there is enough solution to totally submerge the filters. Place the lid on the container and tightly seal.

4.4.4 Clamp the container to the test tube shaker and immobilize the impregnation container in the shaker using a piece of foam rubber and clamp bar. Agitate slowly by adjusting the speed to 60 cycles per minute (knob setting at 3) and leave on for 30 minutes.

4.4.5 Remove the impregnation container from the shaker and decant the impregnation solution. Transfer the stack of filters to a five cm Hirsch funnel and place a sheet of parafilm on the top of the funnel.

4.4.6 Place the funnel into a 500 ml vacuum flask and apply house vacuum (see section 4.3.6). Allow the vacuum to draw off all of the excess wash solution from the stack of filters. The parafilm will be drawn into the funnel and will press over the filter stack to press out excess liquid. When this solution is dripping at a rate of 2 drops/sec., transfer the stack of filters back to the impregnation container and continue with Drying Procedure on Section 4.6.

4.4.7 Set up the vacuum oven as described in Section 4.6. The drying procedure takes five to ten minutes.

4.5 Inspection and Impregnation of TEA filters

4.5.1 Open a box of 47 mm 100 Whatman 31ET Chromatography filters.

4.5.2 Prior to actual impregnation, the TEA filters are washed in a solution of 50% (V/V) methanol and 50% (V/V) DDW. Prepare this solution and add approximately 100 ml to the Teflon impregnation container with approximately 50 filters (make sure it is enough to submerge the filters). Place the lid on the container and seal tightly.

4.5.3 Clamp the container to the test tube shaker and immobilize the impregnation container in the shaker using a piece of foam rubber and clamp bar. Agitate slowly by adjusting the speed to 60 cycles per minute (knob setting at 3) and leave on for 30 minutes.

4.5.4 Remove the impregnation container from the shaker and decant the impregnation solution. Transfer the stack of filters to a five cm Hirsch funnel and place a sheet of parafilm on the top of the funnel.

4.5.5 Place the funnel into a 500 ml vacuum flask and apply house vacuum (see section 4.3.6). Allow the vacuum to draw off all of the excess wash solution from the stack of filters. The parafilm will be drawn into the funnel and will press over the filter stack to press out excess liquid. When this solvent solution is completely squeezed out, transfer the stack of filters back to the impregnation container.

4.5.6 Add approximately 100 ml of TEA impregnation solution, making sure there is enough solution to totally submerge the filters. Place the lid on the container and tightly seal.

4.5.7 Clamp the container to the shaker as in step 4.5.3 and follow the same procedure to agitate the container.

4.5.8 Follow the same procedure in 4.5.4 and 4.5.5 WITH ONE IMPORTANT EXCEPTION. Instead of aspirating all of the impregnation solution from the stack of filters, some residual solution should remain on the filters. Only apply the vacuum on the filters until the liquid stream exiting the funnel reaches approximately 4 drops per second. DO NOT OVER-SQUEEZE THESE IMPREGNATED FILTERS.

4.5.9 Set up the vacuum oven as described in Section 4.6. Dry for five minutes and remove impregnated filters from the vacuum oven. (CAUTION: DO NOT OVER DRY THE FILTERS.)

4.6 Vacuum Oven Drying Procedure

4.6.1 Preheat oven to proper temperature: 30-35□C for citric acid and TEA filters; 60-70□C for K_2CO_3. Turn on vacuum pump. Make sure inlet valve is closed and that there is ice in the trap when drying TEA and Citric Acid filters.

4.6.2 Load filters on top of clean inverted Petri Dishes. Approximately seven 47mm filters and ten 25mm filters can be arranged per Petri Dish. Place Petri dishes into the vacuum oven. Close and latch the door.

4.6.3 Open Vacuum inlet until pressure reaches 20-25 mm Hz. Dry the impregnated filters until they are translucent. This process takes 5 to 10 minutes for K_2CO_3 and Citric Acid filters and 5 minutes for TEA filters. The TEA do not change in appearance. Remove them after 5 minutes.

4.6.4 Close Vacuum inlet and open the air inlet. When the vacuum pressure has decreased to zero (this process takes approximately 2 minutes), remove the petri dishes and filters.

4.6.5 With gloved hands and using tweezers, remove each filter individually and inspect each filter using a bright light table. Make sure there are no holes, wrinkles, torn edges, or foreign materials. Make sure that each filter is uniform in thickness and appearance and that each one is a perfect circle.

4.6.6 Place dried impregnated filters in lots of 100 per batch into plastic boxes with assigned DRI lot ID and impregnation date.

4.6.7 Place filter lots in ziplock bags and store in the refrigerator.

4.7 Data Recording

Complete the first five sections of a Filter Impregnation Log Sheet (Figure 2-1) for each batch of filters. The final sections will be completed by the analyst after the batches are acceptance tested.

In the ACCEPT subdirectory of the D-DRIVE on EAFMAIN (the environmental analysis facility's file server), access the TEA.dbf and append the new DRI Lot Numbers as TEA(Lot Number)A and TEA(Lot Number)B. The analyst will complete the necessary data entry when analysis is complete by filling in the appropriate concentrations.

5.0 QUANTIFICATION

(Not applicable)

6.0 QUALITY CONTROL

6.1 Appearance Check

Check for uniform appearance, even color (white), off color, excessive wetness or dryness, stiff or brittle appearance. Place rejects into a petri dish labeled "rejects" and mark with the batch number.

6.2 Acceptance Testing

Two percent of the filters in each batch of impregnated and dried filters are analyzed for background levels. If filters are stored in separate containers of less than 100 filters, analyze at least one filter from each container.

All of the filters analyzed must contain the levels of ions prescribed below. If results are not within stated limits, the entire batch from which the test filter came fails and is not used for sampling.

- 47mm K_2CO_3 impregnated < 1 μg SO_4^{2-}/filter
- 25mm K_2CO_3 impregnated < 0.28 μg SO_4^{2-}/filter
- 47mm K_2CO_3 impregnated > 19.0 mg K^+/filter
- 25mm K_2CO_3 impregnated > 5.4 mg K^+/filter
- 47mm Citric Acid impregnated < 1 μg NH_4^+/filter
- 47mm TEA impregnated < 1 μg NO_3^-/filter

Results of the blank analyses are summarized in the last 2 sections of the Filter Impregnation Log Sheet (Figure 2-1), and entered into the appropriate acceptance database.

7.0 QUALITY ASSURANCE

(Not applicable)

8.0 REFERENCES

(Not applicable)

APPENDIX A.2

DRI STANDARD OPERATING PROCEDURE — Pages: 397

Date: 11/24/98

Title: Filter Pack Assembly, Disassembly, and Cleaning — Number: 2-110.4

Revision: 4

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the assembly, shipping, and disassembly of filter packs used for aerosol sampling. It also covers the cleaning and storage of the filter holder parts after disassembly.

1.2 Measurement Principle

(Not applicable)

1.3 Measurement Interferences and Their Minimization

(Not applicable)

1.4 Ranges and Typical Values

(Not applicable)

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

(Not applicable)

1.6 Responsibilities of Personnel

All technicians in the laboratory should read and understand the entire standard operating procedure before performing assembly, disassembly, or cleaning of filter packs.

The Laboratory Coordinator is responsible for ensuring that the procedures are properly followed and to deliver the filters for shipping or assembly within the specified time period.

The Quality Assurance Officer of DRI's Energy and Environmental Engineering Center is responsible for determining the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

The QA Officer is also responsible to update this procedure periodically.

1.7 Definitions

No terms used in this procedure require definitions.

1.8 Related Procedures

DRI SOP #2-104.3	Impregnating, Drying, and Acceptance Testing of Filters for Sampling Gases in Air.
DRI SOP #2-105.3	Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling.
DRI SOP #2-106.3	Pre-firing of Quartz Fiber Filters for Carbonaceous Sampling.
DRI SOP #2-102.3	Gravimetric Analysis Procedures.
DRI SOP #2-107.3	Procedures for Light Transmission Analysis.
DRI SOP #2-209.4	Sample Shipping, Receiving, and Chain-of-Custody.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Materials

2.1.l Filter Holders for Particle and Gaseous Sampling

- 46.2 mm filter cassette with screen for $PM_{2.5}$ FRM sampling with Graseby Andersen FRM sampler (Andersen Instruments, Atlanta, GA). Note that Graseby Andersen cassettes will not work in Rupprecht & Patashnick FRM samplers.

- 46.2 mm filter cassette with screen for $PM_{2.5}$ FRM sampling with Rupprecht & Patashnick FRM sampler (Rupprecht & Patashnick, Albany, NY). Note that R&P cassettes will work in other manufacturers' FRM samplers.

- Injection molded Teflon open face inlet (Savillex Corp, Minnetonka, MN).

- Two-part injection molded Teflon inline outlet with a 3/8" fitting and a polypropylene clampnut (Savillex Corp, MN).

- Injection molded Teflon support grids with grooves for o-rings (Atmospheric Technology Inc.).

- Viton o-rings to fit the groove in the support grid.

- 47 mm Nuclepore filter holder with support grid, O-ring, anti-twist ring, and locking ring (Nuclepore, Pleasanton, CA).

- 47 mm Nuclepore multiple holder adapter (Nuclepore, Pleasanton, CA).
- Plastic cap to fit over locking ring. (Brooks and Company, Alameda, CA
- Nuclepore Swin-lok filter holder for aerosol sampling Van Waters and Rogers, Salt Lake City, UT).
- Barcoded labels, 1/2" x 1 3/4" (Avery #5267).
- Wired cardboard mailing tags, approximately l" X 2".

2.1.2 Filter Media

- Teflon 2 μm pore size, 46.2 mm (Whatman, Clifton, NJ) for $PM_{2.5}$ SLAMS FRM sampling – usually provided by state/local agency which obtains them from EPA.
- Teflon 2 μm pore size, 47 mm (Gelman Scientific, Ann Arbor, MI).
- Teflon 2 μm pore size, 37 mm (Gelman Scientific, Ann Arbor, MI)
- Teflon, Zefluor 2 μm pore size, 47 mm (Gelman Scientific, Ann Arbor, MI)
- Citric acid-impregnated Whatman 41 cellulose, 47 mm (Chemtrex, Hillsboro, OR; impregnation performed at DRI).
- K_2CO_3-impregnated Whatman 41 cellulose, 47 mm (Chemtrex, Hillsboro, OR; impregnation performed at DRI).
- Glass fiber filters, Pallflex TX40HI20-WW, 47 mm (Pallflex, Putnam, CT).
- Quartz fiber filters, 2500 QAT-UP, 25 mm (Pallflex, Putnam, CT).
- Quartz fiber filters, 2500 QAT-UP, 37 mm (Pallflex, Putnam, CT).
- Quartz fiber filters, 2500 QAT-UP, 47 mm (Pallflex, Putnam, CT).
- TEA-impregnated, chromatography 31ET filters, 47 mm (Chemtrex, Hillsboro, OR; impregnation performed at DRI).
- Nylon filters, 1.0 μm pore size, 47 mm (Gelman, Ann Arbor, MI).
- Barcoded labels, 1/2 X 1 3/4(Avery #5267).

- Field data sheets.

2.1.3 Barcode Labels

The filter holders and containers are labeled with barcode labels generated using the ANALYSIS program. As shown in Figure 2-1, these labels contain both human- and machine-readable versions of the ID number. For all filter packs except those used for $PM_{2.5}$ FRM sampling, the first two characters of the ID number signify the site, and the third and fourth characters indicate particle size and filter pack type:

ID	Filter Pack Type
TT	PM_{10} Teflon
TQ	PM_{10} Teflon / quartz
RT	$PM_{2.5}$ FRM Teflon
FT	$PM_{2.5}$ Teflon / quartz
FQ	$PM_{2.5}$ quartz / nylon
GK	Glass fiber / citric acid impregnated cellulose / potassium carbonate impregnated cellulose
GQ	Quartz / nylon
GT	TEA impregnated 31ET
DN	Denuded nylon
TN	Teflon / nylon
TK	Teflon / citric acid impregnated cellulose / potassium carbonate impregnated cellulose

The last three characters indicate the Sample ID number.

Figure 2-1. Example of DRI Filter Holder Barcode Labels.

For $PM_{2.5}$ FRM sampling, the first two characters are the Network ID. The third and fourth characters are the Site ID. The fifth and sixth characters are "RT", indicating that the filter pack type is $PM_{2.5}$ FRM Teflon. The seventh character indicates the last digit of the sampling calendar year (e.g., "9" for 1999 or "0" for 2000). The last three characters indicate the Sample ID number.

2.1.4 Equipment

- Flat-tipped tweezers (Millipore, South San Francisco, CA)
- PVC gloves, non-powdered (Fisher, #11-393-26).
- Kaydry towels (Van Waters and Rogers, Salt Lake City, UT).
- PetriSlides, 47 mm (Millipore, #PD15004700).
- Filter cassette containers, 50 mm (Gelman, #7242).
- Drain Disks, 47 mm (Nuclepore, Pleasanton, CA).
- Filter cassette separation tool (Rupprecht & Patashnick, Albany, NY).
- Polystyrene extraction tubes, 15 ml, with screw-cap lids, in racks (Van Waters and Rogers, Salt Lake City, UT)
- Automatic dishwasher.
- Mesh bags (type used for washing fragile items).
- Drying racks or towels.

2.2 Reagents

(Not Applicable)

2.3 Forms

Filter Assignment Log Sheet (Figure 2-2).

Filter Assignment Logsheet

Cond. Date	24hr Date	Weigh Date	Proj Code	Filter Size	Box Number/ DRI Lot Number	FRM Filter Numbers	Assigned IDs (DRI Lots)

Figure 2-2. Filter Assignment Log Sheet.

3.0 CALIBRATION STANDARDS

(Not Applicable)

4.0 PROCEDURES

4.1 General Flow Diagrams

- Assembly (Figure 4-1).
- Disassembly (Figure 4-2).
- Cleaning (Figure 4-3).

4.2 Procedure for Assembly of GK filter packs (Figure 4-4).

Teflon filters used for sampling are weighed before and after sampling. They are stored in labeled PetriSlides before assembly into filter holders, and are returned to the same PetriSlides during filter pack disassembly. All other filters are placed into labeled PetriSlides during disassembly.

4.2.1 Cover area with Kaydry towels

4.2.2 Place the tray containing pre-weighed Teflon filters, the box of K_2C0_3 impregnated filters and the box containing citric acid impregnated filters in the work area.

4.2.3 Place the required filter parts in the work area (see Figure 4-4), attach wire tags, with the barcode label on them, to the complete set of nuts.

4.2.4 Snap the flat grid into the outlet.

4.2.5 Wearing gloves, hold the outlet in one hand and use the flat tipped tweezers to place one potassium carbonate impregnated filter on the outlet. Be sure that the filter fits within the "ears" of the outlet. Snap the support grid, with the O-ring down, into the outlet. Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly, but they must not overlap).

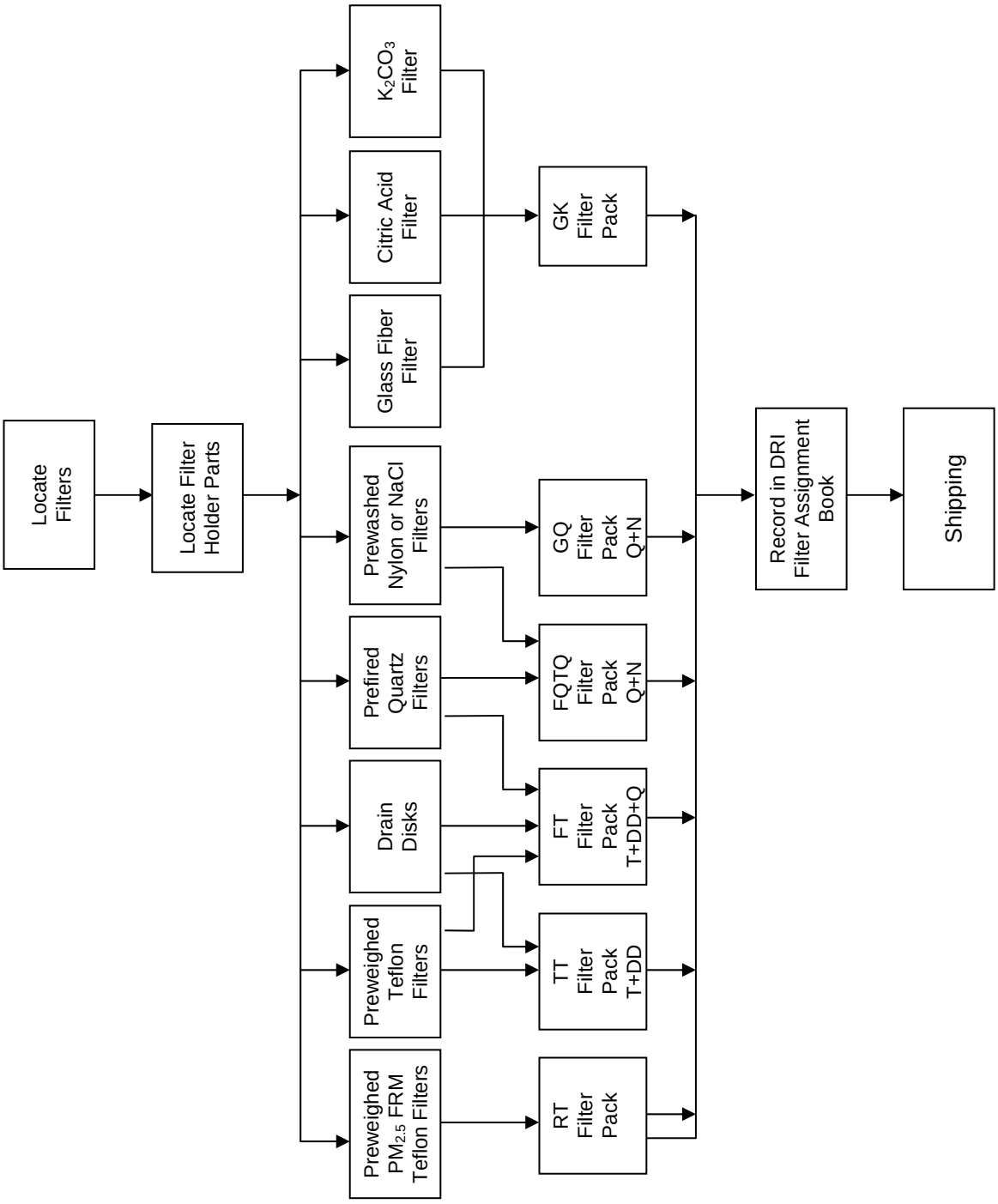


Figure 4-1. DRI Filter Pack Assembly Flow Diagram.

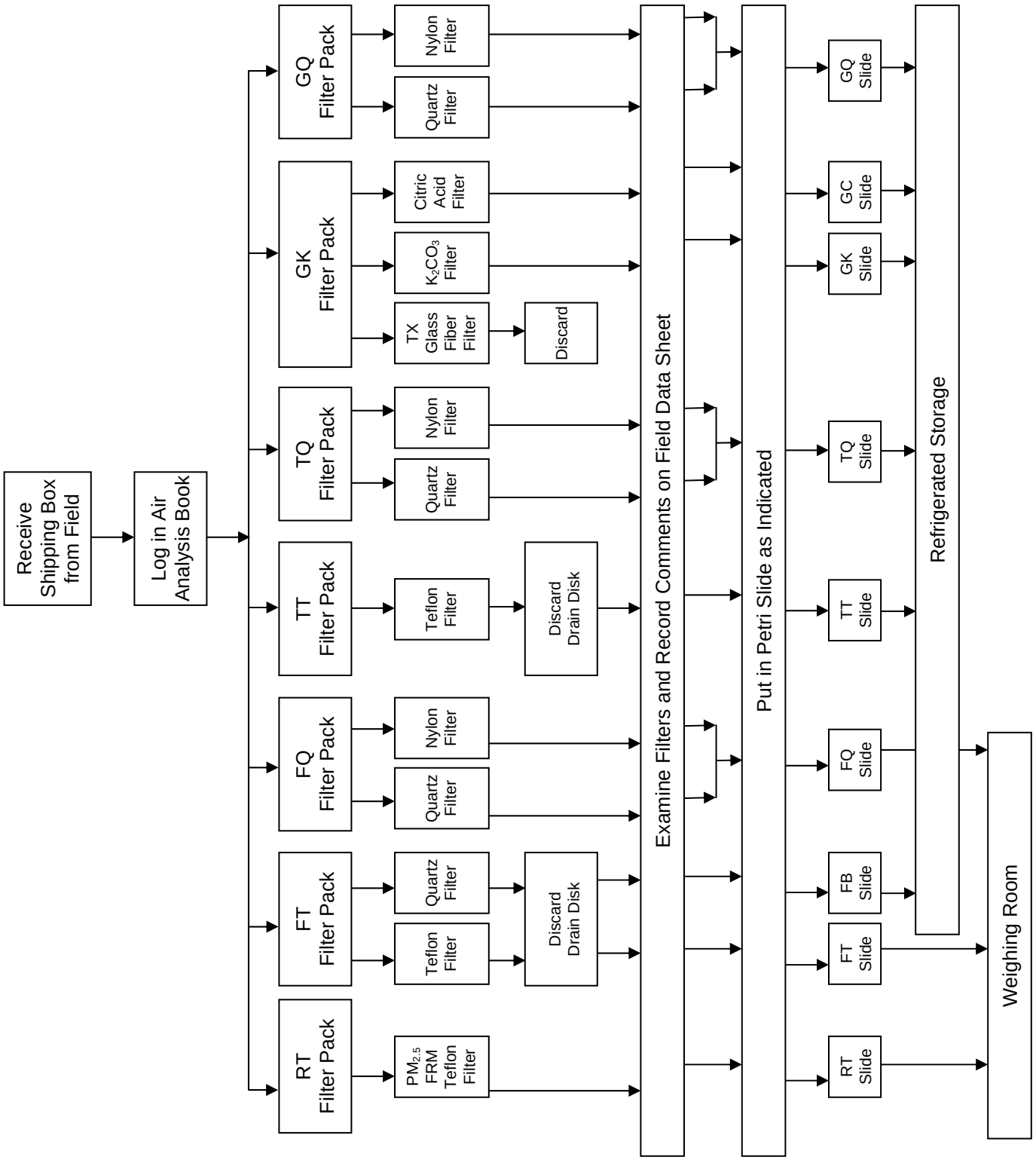


Figure 4-2. DRI Filter Pack Disassembly Flow Diagram.

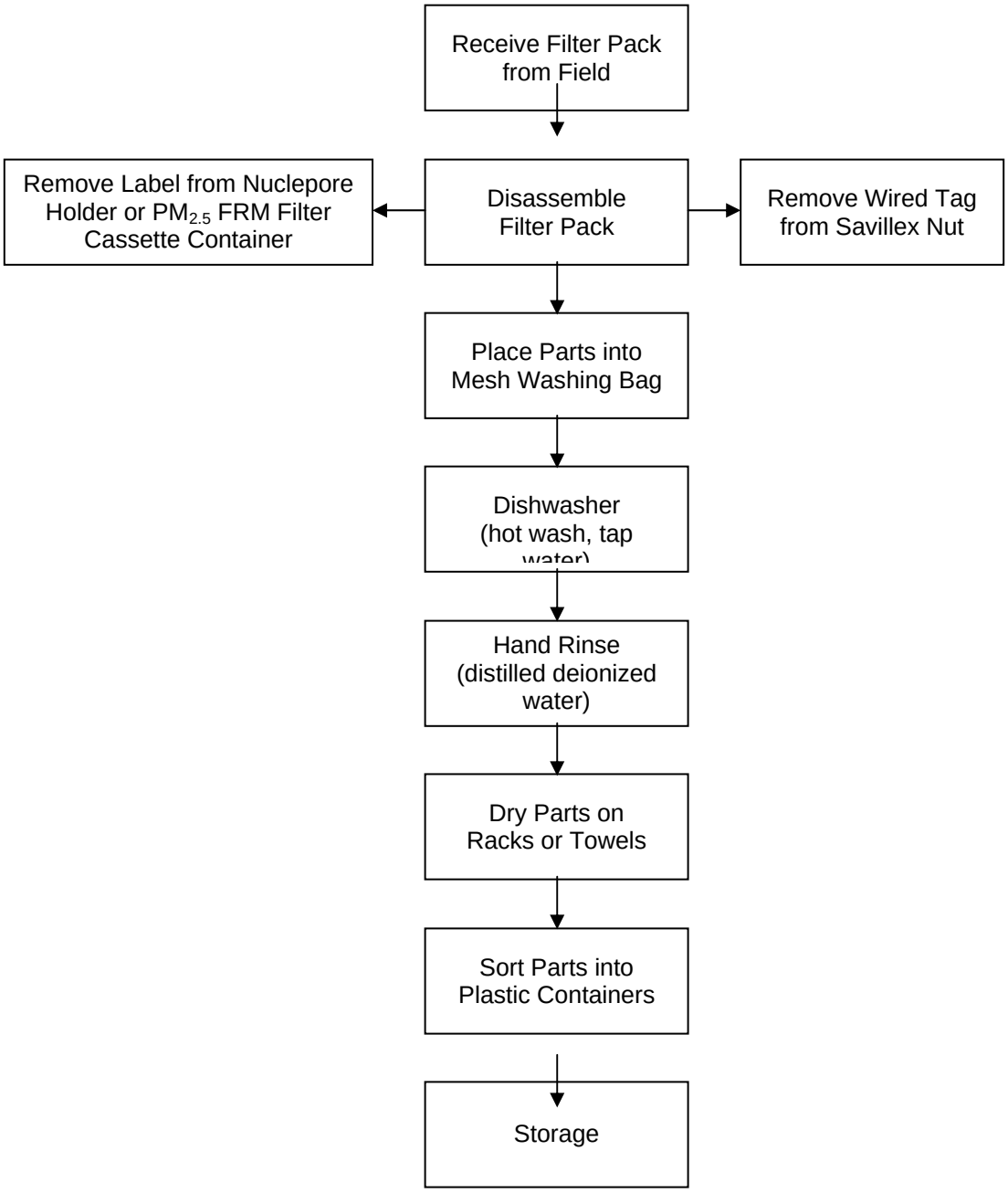


Figure 4-3. Flow Diagram for Filter Holder Cleaning and Storage.

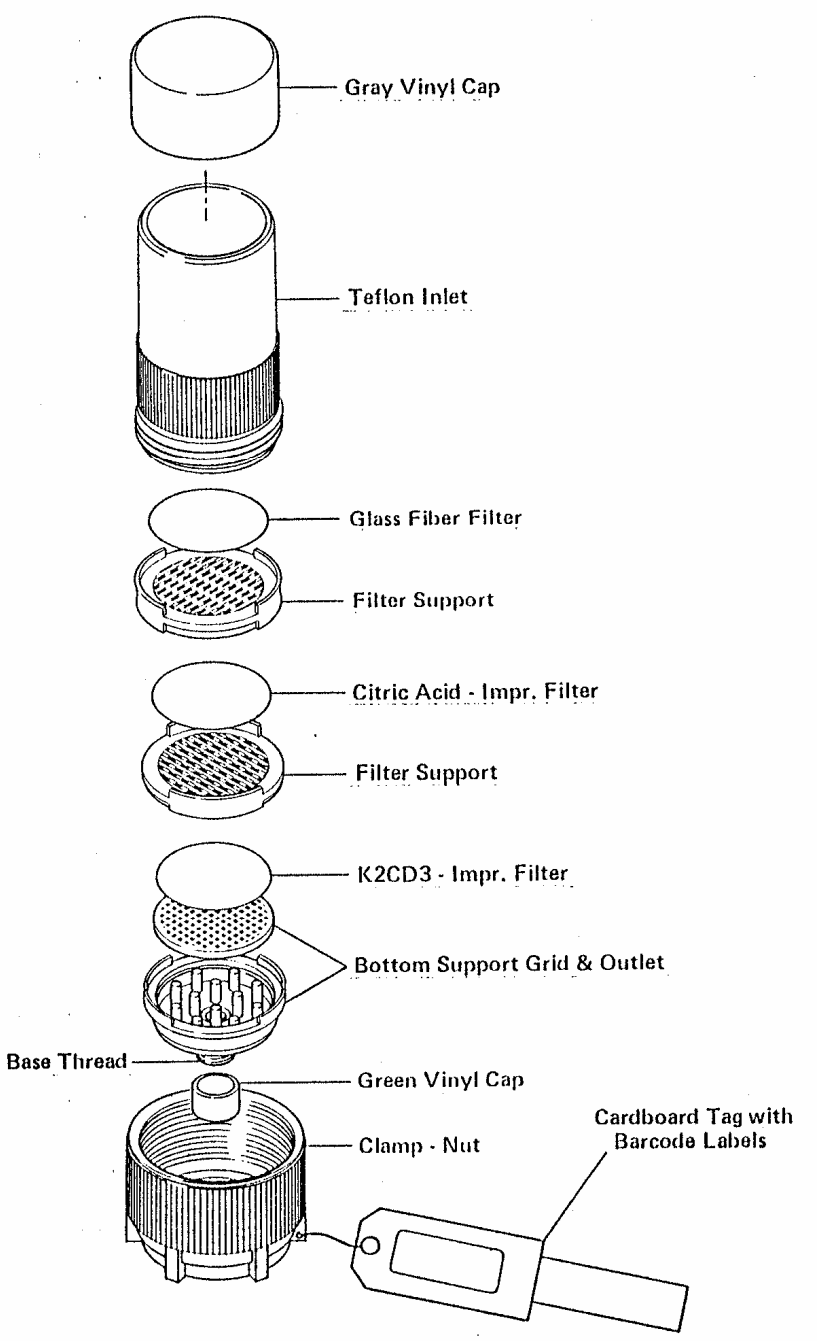


Figure 4-4. Assembly Diagram for GK Filter Packs.

4.2.6 Put the finished first stage on the Kaydry towel. Complete the whole set of filter packs using the potassium carbonate impregnated filters before proceeding with citric acid impregnated filters. This is to ensure that the citric acid and potassium carbonate impregnated filters do not get switched.

4.2.7 Using the tweezers, place a citric acid impregnated filter on the support grid, again being sure that the filter fits within the "ears".

4.2.8 Snap another grid into place, as in 4.2.5.

4.2.9 Hold the assembly tightly with one thumb on the top grid and a finger on the bottom. Insert this assembly into the pre-labeled nut, make sure that the outlet is seated in the nut. Complete the whole set of nuts.

4.2.10 Using the tweezers, carefully place the glass-fiber filter on the top support grid.

4.2.11 Screw the inlet into the nut. When receptacle nut hits/nears the filter, start screwing the nut up to meet the receptacle, being careful not to tear the filter. Look down at the filter to make sure alignment is correct. If the edge of the filter is visible or lifted, loosen the nut, recenter the filter and retighten. If the filter is torn or damaged, replace it.

4.2.12 Place the gray cap on the top end of the inlet.

4.2.13 Place the green cap on the grooved outlet on the bottom of the pack. If the green cap is put on first, air pressure may force the top filter out of position.

4.2.14 After all filter packs are assembled, place them in the designated shipping container.

4.2.15 Record the project, type of filter, lot number of the filter(s) used and the filter ID on the Filter Assignment Log Sheet (Figure 2-2).

4.3 Procedure for Disassembly of GK Filter Packs (Figure 4-4)

4.3.1 Filter Handling Precautions: These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.
- Always wear non-powdered PVC gloves.

- Your breath contains ammonia. Therefore, avoid breathing on any filters, particularly the citric acid-impregnated filters, since they will collect ammonia from your breath.

4.3.2 Cover work area with Kaydry towels.

4.3.3 Place a filter holder awaiting disassembly on one side of work area.

4.3.4 Place three corresponding empty, pre-labeled PetriSlides on the work area. There should be a separate PetriSlide for the Teflon filter, potassium carbonate filter, and the citric acid filter. Be sure the filter ID matches the PetriSlide ID.

4.3.5 Remove the green cap from the outlet and the gray cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment (Figure 4-5).

4.3.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.3.7 Remove the Teflon filter from the top grid and place it in the PetriSlide. Be sure the number of the pack and the PetriSlide correspond. If there is a discrepancy, make a note in the "Comments" section of the filter and unload the filter into the PetriSlide whose number is on the filter holder.

4.3.8 Remove the remaining assembly from the nut by placing a finger on the top and a thumb on the bottom.

4.3.9 Remove the top grid from which the Teflon was removed. The citric acid filter is now exposed. Carefully remove the filter and put it in the corresponding PetriSlide. Place the rest of the filter pack containing the potassium carbonate filter on its nut. Complete all of the citric acid filters before proceeding.

4.3.10 Repeat step 4.3.9 for the potassium carbonate filter.

4.3.11 Store the PetriSlides with the filters in a Ziplock bag in a labeled box in the refrigerator indicated by your supervisor.

DRI Sequential Filter Sampler Field Data Sheet

Network Name: _____ Sampler ID: _____ Date Shipped from DRI: _____ By: _____
Site Name (code): _____ Technician: _____ Date Shipped to DRI: _____ By: _____
Date Received at DRI: _____ By: _____

Filter ID	Port ID	Particle Size[a]	Sampling Date (YYMMDD)	Sampling[b] Period HHMM to HHMM	Elapsed Time (min)		ΔTime(min)	Flow Rate (SCFH)[c]		Flags	Comments
					Start	End		Initial	Final		

[a] Particle Size: Use T for PM_{10}, F for $PM_{2.5}$, and C for $PM_{2.5}$ to PM_{10}
[b] Sampling Period: Circle time zone: Pacific (PST, PDT), Mountain (MST, MDT), Eastern (EST, EDT)
[c] Flow rate: Rotameter reading in Standard Cubic Feet per Hour (SCFH)

Page _____

LAB2 4/5/90

Figure 4-5. Sequential Filter Sampler Field Data Sheet.

4.3.12 Remove wire tags from the nuts and put all filter parts into mesh bags to be washed.

4.4 Procedure for Assembly of GQ Filter Pack (Figure 4-6)

4.4.1 Cover area with Kaydry towels.

4.4.2 Place one box of pre-washed nylon filters and one box of pref-fired quartz filters on the work area.

4.4.3 Place the required filter parts on the work area (see Figure 4-6). Attach wire tags, with the barcode labels on them, to all nuts in the set.

4.4.4 Wearing gloves, snap a support grid, o-ring down, into the outlet. (CAUTION: BE SURE THERE IS NO FLAT GRID IN THE OUTLET). Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly, but they must not overlap.)

4.4.5 Insert the outlet and grid into the pre-labeled nut, being sure that the outlet is seated in the nut.

4.4.6 Using flat-tipped tweezers, place one nylon filter on the support grid, being sure that it fits down within the "ears. Place one quartz filter on top of the nylon filter. Finish the assembly of the filter pack as in steps 4.2.11 to 4.2.15.

4.5 Procedure for Disassembly of GQ Filters (Figure 4-6)

4.5.1 These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.
- Always wear non-powdered PVC gloves when disassembling filter holders.

4.5.2 Cover work area with Kaydry towels.

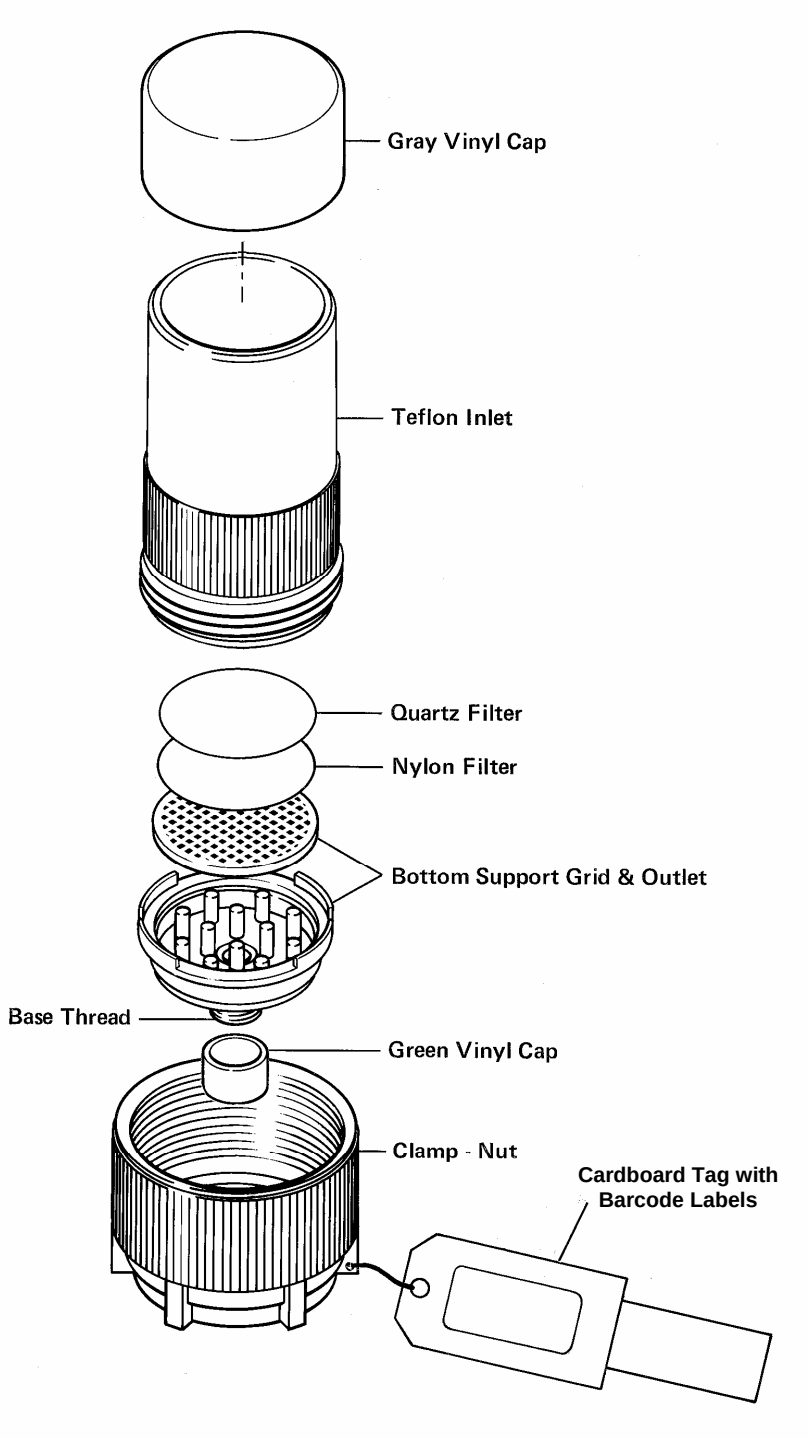


Figure 4-6. Assembly Diagram for GQ Filter Packs.

4.5.3 Place a filter holder awaiting disassembly on one side of work area.

4.5.4 Place a pre-labeled PetriSlide to hold the filters on the work area. Be sure the numerical ID on the PetriSlide and the filter pack are identical.

4.5.5 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet. Push the outlet from the bottom until the quartz-nylon filter pack can be accessed.

4.5.6 Remove the quartz-nylon pack from the grid. Inspect the filters for the presence of any unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment (Figure 4-5).

4.5.7 Place the filter pack into the appropriate PetriSlide, and cover the slide. Unload all filter packs received.

4.5.8 Store the PetriSlides with the filters in a Ziplock bag in a labeled box in the refrigerator as instructed by the supervisor.

4.5.9 Remove the wire tags from the nuts and put all filter parts in mesh bags to be washed.

4.6 Procedure for Assembling FT Filter Pack (Figure 4-7)

4.6.1 Cover area with Kaydry Towels.

4.6.2 Place the required Nuclepore filter parts on the work area (Figure 4-7). Wearing gloves, label the filter holder base using a label from the barcode sheet. Place the label on the side of the holder, making sure that it is securely attached.

4.6.3 Place a box of pref-fired quartz filters, a bag of drain disks and a PetriSlide containing a Teflon filter on the work area. (CAUTION: BE SURE THAT THE LABEL ON THE PETRISLIDE CORRESPONDS TO THE LABEL ON THE FILTER HOLDER BASE).

4.6.4 Put an O-ring around the support grid and snap it into the filter holder base, making sure that the smooth side of the grid is up.

4.6.5 Using flat-tipped tweezers, carefully place one quartz filter on the grid, one drain disk on the quartz filter and the Teflon filter on the drain disk.

4.6.6 Place an anti-twist ring on the filters making sure that the “ears” of the anti-twist ring fit into the “ears” of the filter holder base in such a way the ring can not be twisted on the base. Double check before proceeding.

4.6.7 Screw the ring onto the filter holder base being careful not to dislodge the anti-twist ring.

4.6.8 Unscrew the ring about one-quarter turn and retighten it. This will usually seat the anti-twist ring if it is not already seated.

4.6.9 Cover filter pack assembly with red vinyl cap.

4.6.10 When all filter packs are assembled, record the DRI lot ID's in the Filter Assignment Notebook.

4.7 Procedure for Disassembling FT Filter Pack (Figure 4-7)

4.7.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.
- Always wear non-powdered PVC gloves when disassembling filter packs.

4.7.2 Cover work area with Kaydry towels.

4.7.3 Place a filter holder awaiting disassembly on one side of work area.

4.7.4 Place the corresponding empty FT and FB PetriSlides on the work area. Remove lids. (CAUTION: BE SURE THAT THE LABEL ON THE PETRISLIDES CORRESPOND WITH THE LABEL ON THE FILTER HOLDER BASE. If it does not, write a comment on the field data sheet and unload into the proper slide).

4.7.5 Remove the red cap.

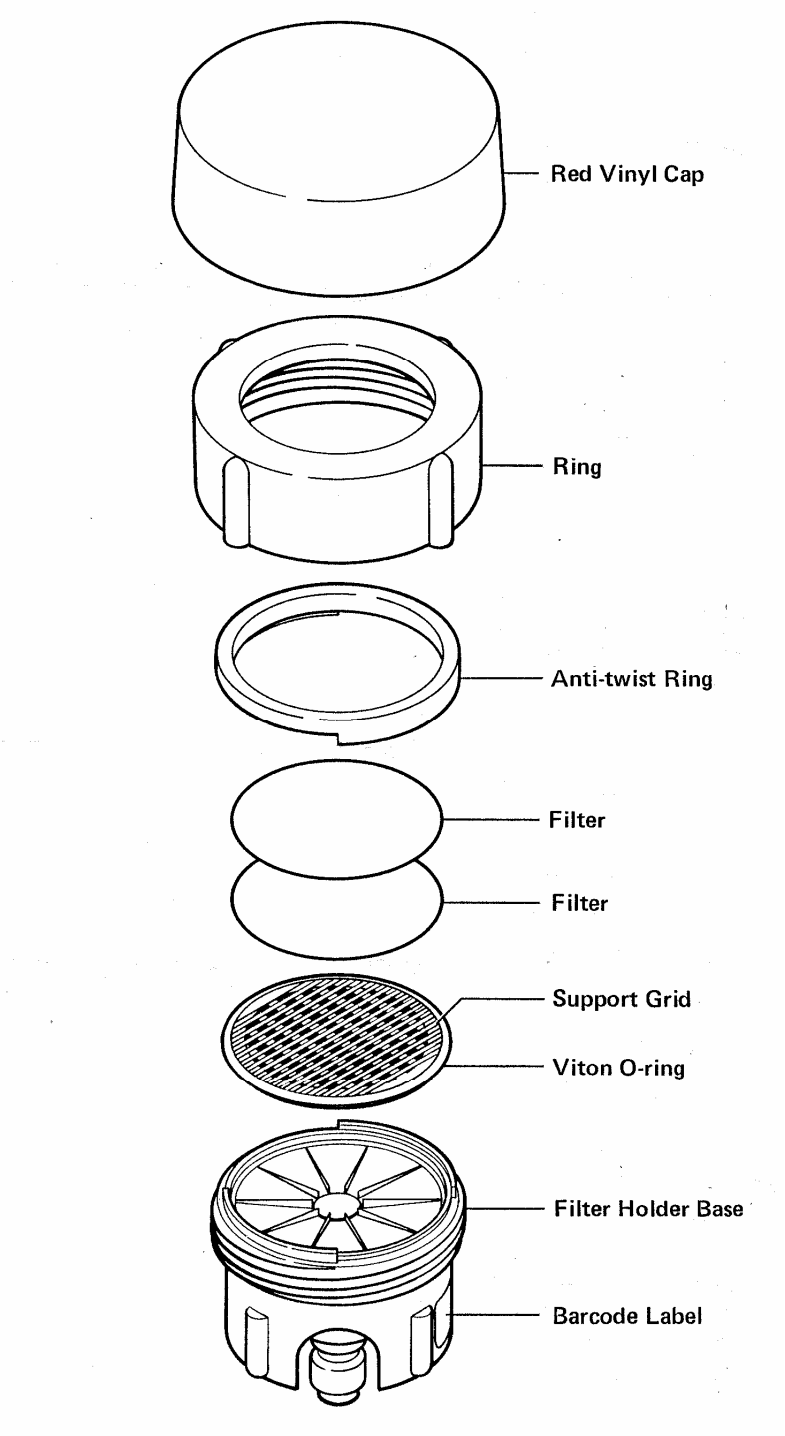


Figure 4-7. Assembly Diagram for FT, FQ, TT, and TQ Filter Packs.

4.7.6 Unscrew the ring from the filter holder base. Carefully lift off the anti-twist ring and place the Teflon filter into the FT PetriSlide. Discard the drain disk and place the quartz filter into the FB PetriSlide. Put the lids on the PetriSlides. Record any unusual findings about the quartz and Teflon filters on the field data sheet returned with the shipment (Figure 4.5).

4.7.7 Remove the label from the filter holder and place all parts into a mesh bag so they can be washed.

4.8 Procedure for Assembly of FQ Filter Packs (Figure 4-7)

4.8.1 Cover the work area with Kaydry towels.

4.8.2 Place the required Nuclepore filter parts on the work area (Figure 4-7). Wearing gloves label the filter holder base using a label from the barcode sheet. Place the label on the side of the holder, making sure that it is securely attached.

4.8.3 Place a box of pref-fired quartz filters and a box of nylon filters in the work area.

4.8.4 Put an O-ring around the support grid and snap it into the filter holder base, making sure that the smooth side is up.

4.8.5 Place one nylon filter on the support grid and one quartz filter on top of it.

4.8.6 Place an anti-twist ring on the filters making sure that the “ears” of the anti-twist ring fit into the “ears” of the filter holder base in such a way the ring can not be twisted on the base. Double check before proceeding.

4.8.7 Screw the ring onto the filter holder base being careful not to dislodge the anti-twist ring.

4.8.8 Unscrew the ring about one-quarter turn and retighten it. This will usually seat the anti-twist ring if it is not already seated.

4.8.9 Cover filter pack assembly with red vinyl cap.

4.8.10 When all filter packs are assembled, record the DRI lot ID’s in the Filter Assignment Notebook.

4.9 Procedure for Disassembly of FQ Filter Packs (Figure 4-7)

4.9.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme caution must be used to avoid

contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.
- Always wear non-powdered PVC gloves when disassembling filter holders.

4.9.2 Cover work area with Kaydry towels.

4.9.3 Place a filter holder awaiting disassembly on one side of work area.

4.9.4 Place the corresponding empty FQ PetriSlide in the work area. (CAUTION: BE SURE THAT THE LABEL ON THE PETRISLIDE CORRESPONDS TO THE LABEL ON THE FILTER HOLDER AND TO THE NUMBER ON THE FIELD DATA SHEET. If it does not, write a comment on the field data sheet and unload into the correct PetriSlide.)

4.9.5 Remove the red cap.

4.9.6 Unscrew the ring from the filter holder base. Carefully lift off the anti-twist ring and put the quartz-nylon filter pack into the FQ PetriSlide. Put the lid on the PetriSlide. Record any unusual findings on the field data sheet returned with the shipment (Figure 4-5).

4.9.7 Remove the label from the filter holder and place all parts into a mesh bag so they can be washed.

4.10 Procedure for Assembly of TT Filter Packs (Figure 4-7)

4.10.1 Cover area with Kaydry Towels.

4.10.2 Place the required filter parts on the work area (Figure 4-7). Wearing gloves, label the filter holder base using a label from the barcode sheet. Place the label on the side of the holder, making sure that it is securely attached.

4.10.3 Place the PetriSlide containing the TT filter and the bag of drain disks in the work area. (CAUTION: BE SURE THAT THE LABEL ON THE PETRISLIDE CORRESPONDS TO THE LABEL ON THE FILTER HOLDER).

4.10.4 Put an O-ring around the support grid and snap it into the filter holder base, making sure that the smooth side is up.

4.10.5 Place one drain disk on the support grid and put the Teflon filter on top of it

4.10.6 Complete assembly as in 4.6.6 to 4.6.10.

4.11 Procedure for Disassembly of TT Filter Packs (Figure 4-7)

4.11.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.
- Always wear non-powdered PVC gloves when disassembling filter packs.

4.11.2 Cover work area with Kaydry towels.

4.11.3 Place a filter holder awaiting disassembly on one side of work area.

4.11.4 Place the corresponding empty TT PetriSlide in the work area. (CAUTION: BE SURE THAT THE LABEL ON THE PETRISLIDE CORRESPONDS TO THE LABEL ON THE FILTER HOLDER AND THE FIELD DATA SHEET. If it does not, write a comment on the field data sheet and unload into the correct PetriSlide.)

4.11.5 Remove the red cap.

4.11.6 Unscrew the ring from the filter holder base. Carefully lift off the anti-twist ring and put the Teflon filter into the PetriSlide. Discard the drain disk. Put the lid on the PetriSlide. Record any unusual findings on the field data sheet returned with the shipment (Figure 4-5).

4.11.7 Remove the label from the filter holder and place all parts into a mesh bag so they can be washed.

4.12 Procedure for Assembly of TQ Filter Packs (Figure 4-7)

4.12.1 Cover the work area with Kaydry towels.

4.12.2 Place the required filter parts on the work area (Figure 4-7). Wearing gloves label the filter holder base using a label from the barcode sheet. Place the label on the side of the holder, making sure that it is securely attached.

4.12.3 Place a box of pref-fired quartz filters and a box of nylon filters in the work area.

4.12.4 Put an O-ring around the support grid and snap it into the filter holder base, making sure that the smooth side is up.

4.12.5 Place one nylon filter on the support grid and one quartz filter on top of it.

4.12.6 Place an anti-twist ring on the filters making sure that the "ears" of the anti-twist ring fit into the "ears" of the filter holder base in such a way the ring can not be twisted on the base. Double check before proceeding.

4.12.7 Screw the ring onto the filter holder base being careful not to dislodge the anti-twist ring.

4.12.8 Unscrew the ring about one-quarter turn and retighten it. This will usually seat the anti-twist ring if it is not already seated.

4.12.9 Cover filter pack assembly with red vinyl cap.

4.12.10 When all filter packs are assembled, record the DRI lot ID's in the Filter Assignment Log Sheet.

4.13 Procedure for Disassembly of TQ Filter Packs (Figure 4-7)

4.13.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme caution must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.
- Always wear non-powdered PVC gloves when disassembling filter holders.

4.13.2 Cover work area with Kaydry towels.

4.13.3 Place a filter holder awaiting disassembly on one side of work area.

4.13.4 Place the corresponding empty FQ PetriSlide in the work area. (CAUTION: BE SURE THAT THE LABEL ON THE PETRISLIDE CORRESPONDS TO THE LABEL ON THE FILTER HOLDER AND THE NUMBER ON THE FIELD DATA SHEET. If it does not, write a comment on the field data sheet and unload the filter into the correct PetriSlide.)

4.13.5 Remove the red cap.

4.13.6 Unscrew the ring from the filter holder base. Carefully lift off the anti-twist ring and put the quartz-nylon filter pack into the FQ PetriSlide. Put the lid on the PetriSlide. Record any unusual findings on the field data sheet returned with the shipment (Figure 4-5).

4.13.7 Remove the label from the filter holder and place all parts into a mesh bag so they can be washed.

4.14 Procedure for Assembly of TK filter packs (Figure 4-8)

Teflon filters used for sampling are weighed before and after sampling. They are stored in labeled petri dishes before assembly into filter holders, and are returned to the same petri dishes during filter pack disassembly. All other filters are placed into extraction tubes during disassembly.

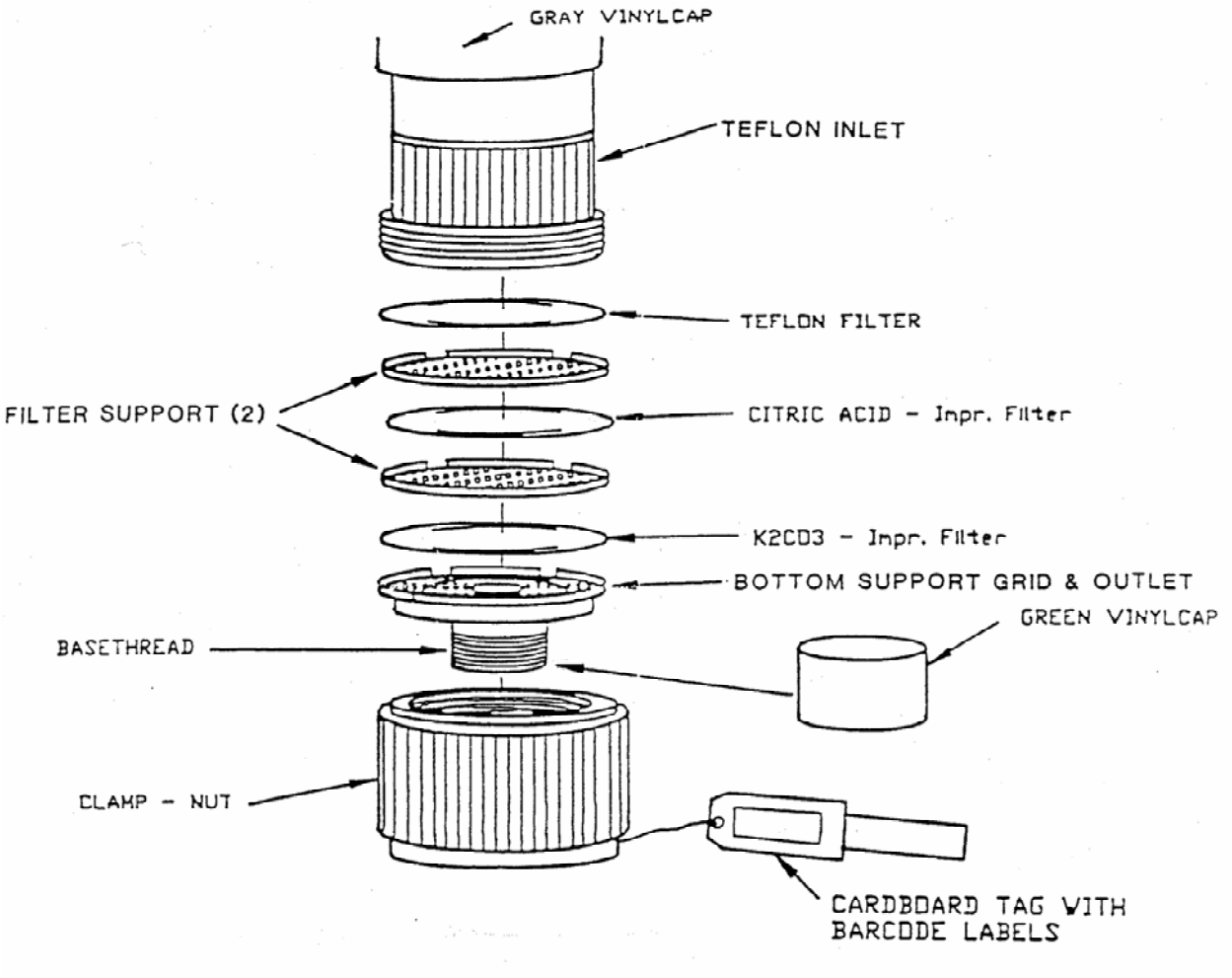


Figure 4-8. Assembly Diagram for TK Filter Packs.

4.14.1 Cover area with Kay-Dry towels.

4.14.2 Place the tray containing pre-weighed Teflon filters, the box of K_2CO_3 impregnated filters and the box containing citric acid impregnated filters in the work area.

4.14.3 Place the required filter parts in the work area (see Figure 4-8), attach wire tags, with the barcode label on them, to the complete set of nuts.

4.14.4 Snap the flat grid into the base.

4.14.5 Wearing gloves, hold the outlet in one hand and use the flat tipped tweezers to place one potassium carbonate impregnated filter on the outlet. Be sure that the filter fits within the "ears" of the outlet. Snap the support grid, with the O-ring down, into the outlet. Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly).

4.14.6 Put the finished first stage on the Key-Dry towel. Complete the whole set of filter packs using the potassium carbonate impregnated filters before proceeding with citric acid impregnated filters. (This is to ensure that the citric acid and potassium carbonate impregnated filters do not get switched).

4.14.7 Using the tweezers, place a citric acid impregnated filter on the support grid again, being sure that the filter fits within the "ears".

4.14.8 Snap another grid into place, as in 4.14.6.

4.14.9 Hold the assembly tightly with one thumb on the top grid and a finger on the bottom. Insert this assembly into the prelabeled nut, make sure that the outlet is seated in the nut. Complete the whole set of nuts.

4.14.10 Using the tweezers, carefully place the Teflon filter on the top support grid. (CAUTION: BE SURE THAT THE ID ON THE WIRE TAG AND THE PETRI SLIDE LABEL ARE IDENTICAL).

4.14.11 Screw the inlet into the nut, being careful not to tear the filter. Look down at the filter to make sure alignment is correct.

4.14.12 Place the grey cap on the top end of the inlet.

4.14.13 Place the green cap on the grooved outlet on the bottom of the pack. If the green cap is put on first, air pressure may force the top filter out of position.

4.14.14 Place the filter pack in the shipping container.

4.14.15 Record the project, type of filter, lot number of the filter(s) used and the filter ID on the chain-of-custody sheet (Figure 2-2).

4.15 Procedure for Disassembly of TK Filter Packs (Figure 4-8)

4.15.1 Filter Handling Precautions: These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.
- Always wear PVC gloves.
- Your breath contains ammonia. Therefore, avoid breathing on any filters, particularly the citric acid-impregnated filters, since they will collect ammonia from your breath.

4.15.2 Cover work area with Kay Dry towels.

4.15.3 Place a filter holder awaiting disassembly on one side of work area.

4.15.4 Place the corresponding empty, prelabeled petri slide and prelabeled extraction tube on the work area.

4.15.5 Remove the green cap from the outlet and the grey cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment (Figure 4-5).

4.15.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.15.7 Remove the Teflon filter from the top grid. Inspect the filter for the presence of any other unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment of filters (Figure 4-5).

4.15.8 Place the Teflon filter in the appropriate petri slide. Place the cover on the container. Remove the remaining assembly from the nut by placing a finger on the top and a thumb on the bottom.

4.15.9 Remove the top grid from which the Teflon filter was removed. The citric acid filter is now exposed. To insert the filter into the tube, place it sample side up, on an inverted petri slide. Using a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside of the fold. Then insert it into the tube. Cap the tube. Clean inverted petri slide, glass rod and tweezers before continuing on with next filter.

4.15.10 Repeat step 4.15.9 for the potassium carbonate filter. (CAUTION: MAKE SURE THE FILTERS ARE PLACED IN THE CORRECT TEST TUBES SINCE CITRIC ACID AND K_2CO_3-IMPREGNATED FILTERS LOOK ALIKE.)

4.15.11 Store the containers with the filters in a refrigerator as instructed by your supervisor.

4.15.12 Remove wire tags from the nuts and put all filter parts into a mesh bag to be washed.

4.16 Procedure for Assembly of DN Filter Pack (Figure 4-9)

4.16.1 Cover area with Kay Dry towels.

4.16.2 Place the box of prewashed nylon filters on the work area.

4.16.3 Place the required filter parts on the work area (see Figure 4-9). Attach wire tags, with the barcode labels on them, to all nuts in the set.

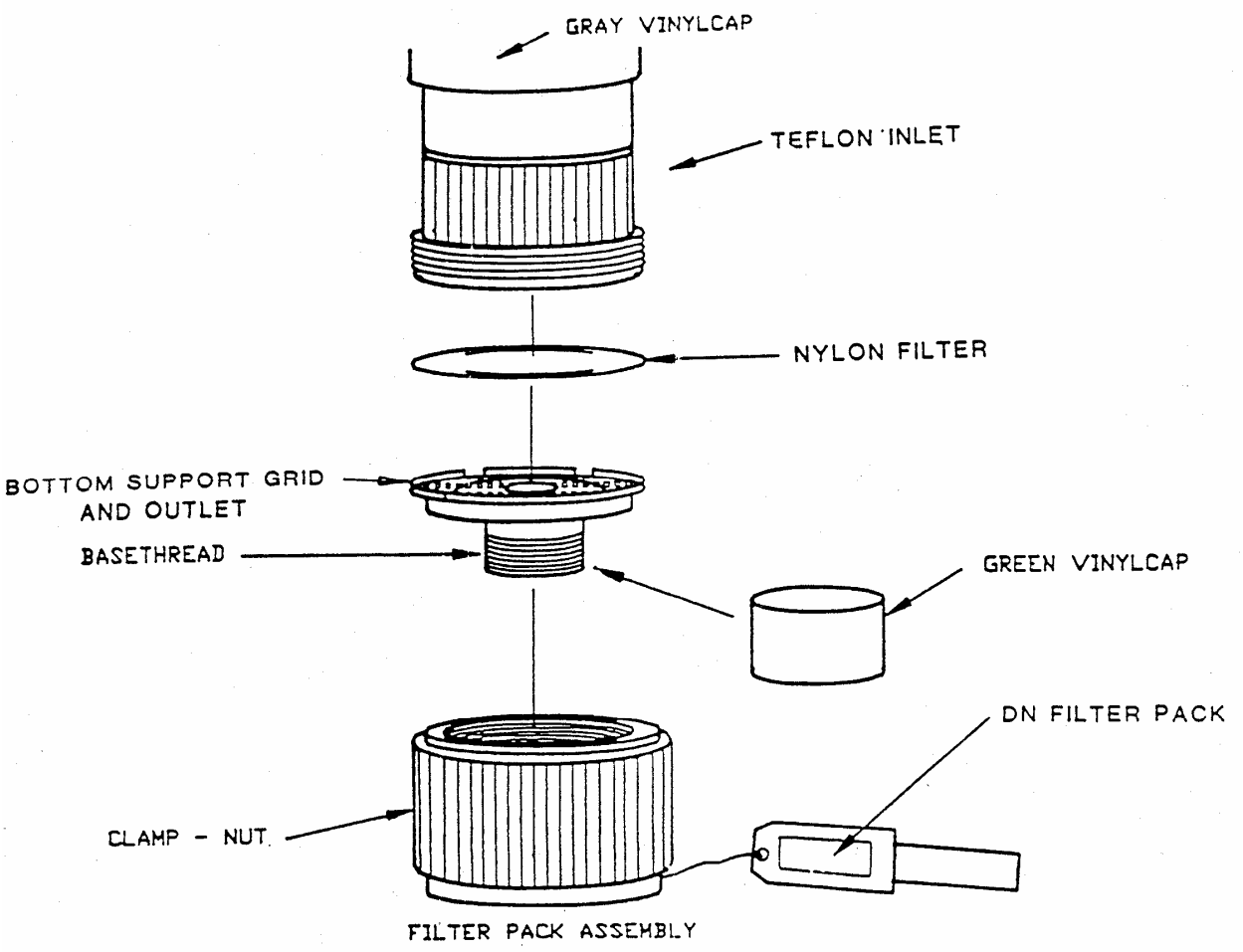


Figure 4-9. Assembly Diagram for DN Filter Packs.

4.16.4 Wearing gloves, snap a support grid, o-ring down, into the outlet. (CAUTION: BE SURE THERE IS NO FLAT GRID IN THE BASE). Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly.)

4.16.5 Insert the outlet and grid into the prelabeled nut, being sure that the outlet is seated in the nut.

4.16.6 Using flat-tipped tweezers, place one nylon filter on the support grid, being sure that it fits down within the "ears". Finish the assembly of the filter pack as in steps 4.2.11 to 4.2.15.

4.17 Procedure for Disassembly of DN Filters (Figure 4-9)

4.17.1 These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.
- Always wear PVC gloves when disassembling filter holders.

4.17.2 Cover work area with Kay Dry towels.

4.17.3 Place a filter holder awaiting disassembly on one side of work area.

4.17.4 Place a prelabeled extraction tube to hold the filter on the work area.

4.17.5 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet. Push the outlet from the bottom until the nylon filter can be accessed.

4.17.6 Remove the single nylon filter from the grid. Inspect the filter for the presence of any unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment (Figure 4-5).

4.17.7 Place the nylon filter into the appropriate test tube as in 4.3.9, and cap the tube.

4.17.8 Store the container with the filter in a refrigerator as instructed by your supervisor.

4.17.9 Remove the wire tags from the nuts and put all filter parts in mesh bags to be washed.

4.18 Procedure for Assembling TN Filter Pack (Figure 4-10)

4.18.1 Cover area with Kay Dry Towels.

4.18.2 Place the box of prewashed nylon filters and the tray of preweighed Teflon filters on the work area.

4.18.3 Place the required filter parts on the work area (Figure 4-10).

4.18.4 Wearing gloves, snap a support grid, o-ring down, into the outlet. (CAUTION: BE SURE THERE IS NO FLAT GRID IN THE BASE). Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly.)

4.18.5 Using flat-tipped tweezers, carefully place one nylon filter on the support grid being sure that it fits down between the "ears".

4.18.6 Snap another support grid, O-ring down, on top of the outlet and nylon filter. Hold the assembly tightly with one thumb on the top grid and a finger on the bottom. Insert this assembly into the prelabled nut.

4.18.7 Load the Teflon filter and finish the assembly as in 4.2.11 to 4.2.15. (CAUTION: BE SURE THAT THE ID ON THE WIRE TAG AND THE PETRI SLIDE ARE IDENTICAL).

4.19 Procedure for Disassembling TN Filter Pack (Figure 4-10)

4.19.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

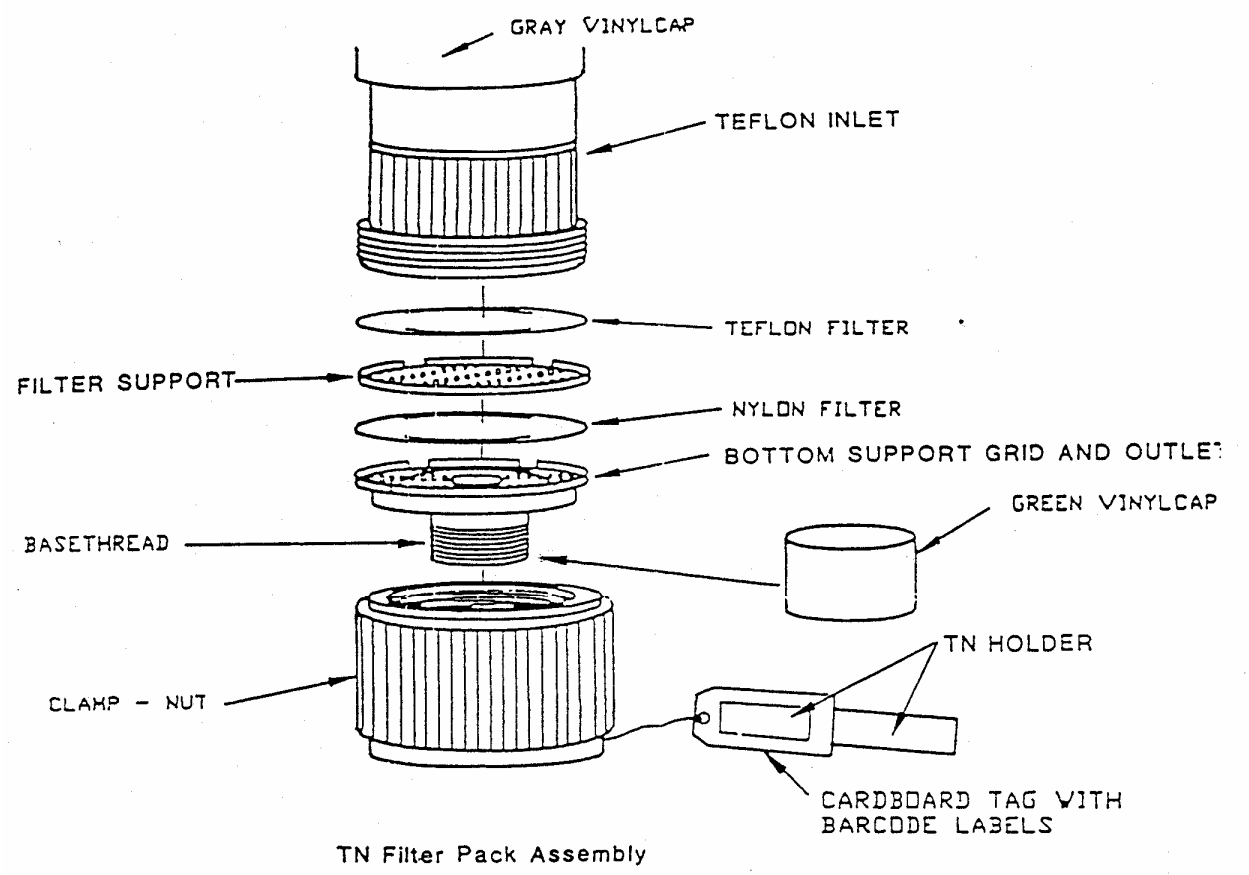


Figure 4-10. Assembly Diagram for TN Filter Packs.

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.
- Your breath contains ammonia. Therefore, avoid breathing on any filters.
- Always wear PVC gloves when disassembling filter packs.

4.19.2 Cover work area with Kay Dry towels.

4.19.3 Place a filter holder awaiting disassembly on one side of work area.

4.19.4 Place the corresponding empty petri dish and prelabeled extraction tube on the work area.

4.19.5 Remove the green cap from the outlet and the grey cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment (Figure 4-5).

4.19.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.19.7 Remove the Teflon filter from the top grid. Inspect the filter for the presence of any unusual conditions. Note these conditions on the Field Data Sheet that was returned with the shipment (Figure 4-5).

4.19.8 Place the filter in the appropriate petri slide. Place the cover on the container. (CAUTION: BE SURE THAT THE ID ON THE WIRE TAG AND THE PETRI SLIDE ARE IDENTICAL).

4.19.9 Remove the grid and outlet in one piece from the nut. This is accomplished by putting a thumb on the threaded outlet and a finger on the support grid. Push the assembly up out of the nut until it can be taken out in one piece.

4.19.10 Separate the support grid from the outlet, exposing the nylon filter.

4.19.11 Place the nylon filter into the appropriate extraction tube as in 4.3.7.

4.19.12 Store the containers with the filters in a refrigerator as instructed by your supervisor.

4.19.13 Remove wire tags from nuts and put all parts into mesh bags to be washed.

4.20 Procedure for Assembly of GT Filter Packs (Figure 4-11)

4.20.1 Cover the work area with Kay Dry towels.

4.20.2 Place the box of TX40HI20 filters and the box of TEA-impregnated filters on the work area.

4.20.3 Place the required filter parts on the work area (see Figure 4-11). Attach the wire tags, with the barcode label on them, to all the nuts in the set.

4.20.4 Wearing gloves, snap the flat grid into the outlet.

4.20.5 Holding the outlet in one hand, use flat-tipped tweezers to place two TEA-impregnated filters on the outlet, making sure that they sit down between the "ears".

4.20.6 Snap the support grid, with the o-ring down, into the outlet. Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly).

4.20.7 Hold the assembly firmly with a thumb on the top grid and a finger on the bottom. Insert this assembly into the prelabeled nut, being sure that the base is seated in the nut.

4.20.8 Using the tweezers, place one TX40HI20 filter on the support grid. The Teflon (non-shiny) side should be facing upward.

4.20.9 Finish the assembly of the filter pack as in steps 4.2.11 to 4.2.15.

4.21 Procedure for Disassembly of GT Filter Packs (Figure 4-11)

4.21.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme caution must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.
- Always wear nylon gloves when disassembling filter holders.

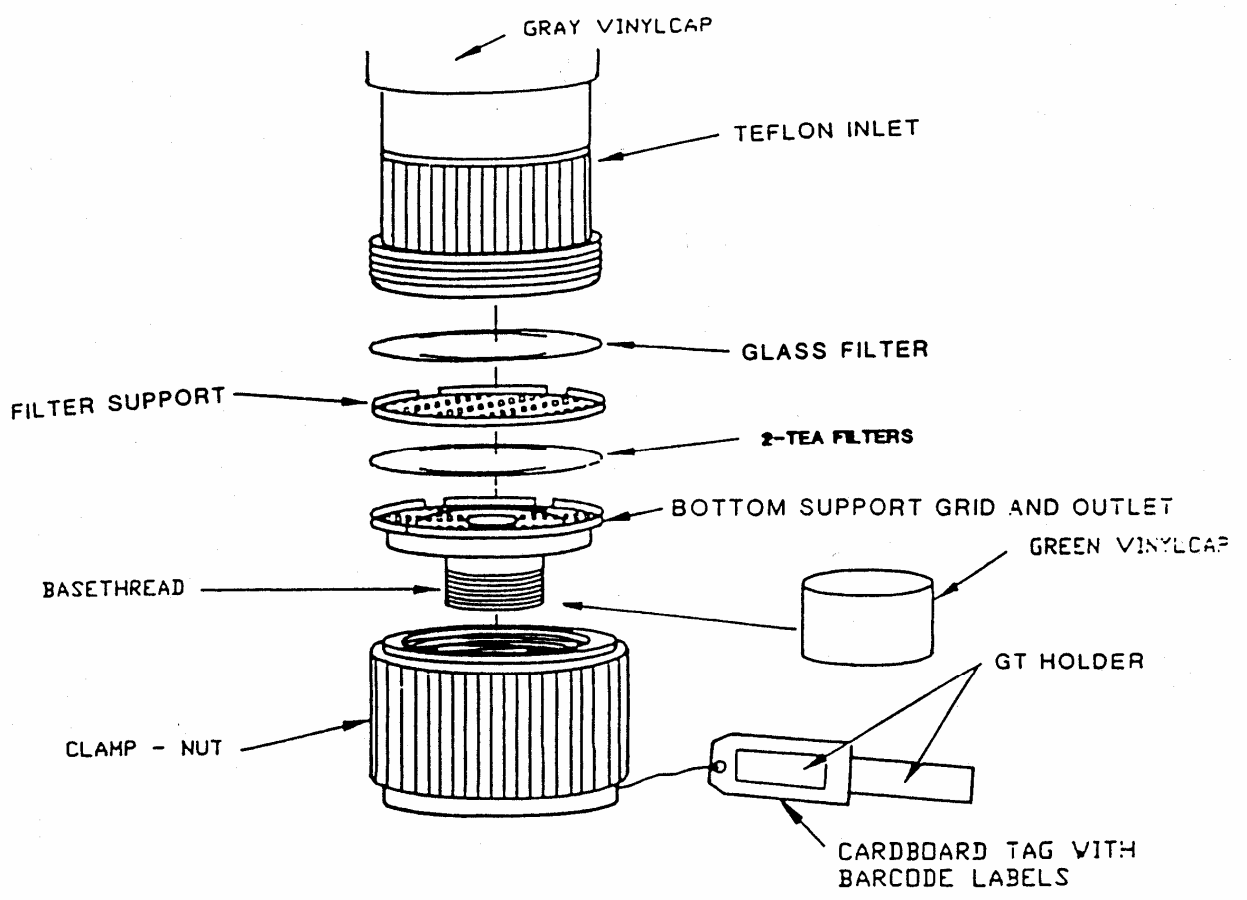


Figure 4-11. Assembly Diagram for GT Filter Packs.

4.21.2 Cover work area with Kay Dry towels.

4.21.3 Place a filter holder awaiting disassembly on one side of work area.

4.21.4 Place the prelabeled extraction tubes on the work area.

4.21.5 Remove the green cap from the outlet and the grey cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment (Figure 4-5).

4.21.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.21.7 Remove the single glass filter from the top grid and dispose of properly. Remove the remaining assembly from the nut while holding firmly to the top and bottom.

4.21.8 Separate the support grid from the outlet, exposing the two TEA-impregnated filters.

4.21.9 Remove the TEA filters from the bottom grid. Inspect the filters for any unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment.

4.21.10 Fold the two TEA filters together, do not separate them. Place into the appropriate test tube as in 4.3.7.

4.21.11 Store the containers with the filters in a refrigerator as instructed by your supervisor.

4.22 Procedure for Assembly of RT Filter Pack (Figure 4-12)

4.22.1 Cover the work area with Kay Dry towels.

4.22.2 Place the Petri slides containing labeled 46.2 mm Teflon filters and the cassette containers on the work area.

4.22.3 Place the required filter parts on the work area. Note that filter cassettes for Graseby Andersen and most other $PM_{2.5}$ FRM samplers will not work in Rupprecht & Patashnick (R&P) $PM_{2.5}$ FRM samplers. However, filter cassettes for R&P $PM_{2.5}$ FRM samplers can be used in other samplers.

4.22.4 Wearing gloves, put the stainless steel support screen into the bottom section of the cassette with the screen ID (if any) facing down.

4.22.5 Holding the bottom section of the cassette in one hand, use flat-tipped tweezers to place a 46.2 mm ringed Teflon filter in the bottom section on top of the screen. The filter ring is facing up.

4.22.6 Place the upper section of the cassette onto the bottom section. Press down along the top rim of the upper section until the upper section fits snugly onto the bottom. Write the sampler magazine sequence number, if any, on the cassette using a "Sharpie" marker. Enter the sequence number on the field data sheet (see Figure 4-12).

4.22.7 Place the assembled filter cassette into the bottom half of the filter cassette container. Then snap the upper half of the container over the bottom half, and place a rubber band around the container to keep the container closed.

4.22.8 Place two bar code labels (one with the filter ID, and the other with the filter cassette screen ID) on top half of the filter cassette container. Mark the magazine sequence number, if any, on the container.

4.22.9 After the filter packs are assembled and put in containers, sort them into groups by site and sampler.

4.22.10 Enter filter IDs, cassette screen IDs, and sampler magazine sequence number on the field data sheet with one sheet for each set of filters per site/sampler. The number of filters in a set is based on sampling frequency and shipping schedule. The number in each set is provided by the Principal Investigator or Project Manager. Complete the initial information for the DRI laboratory on the data sheet.

4.23 Procedure for Disassembly of RT Filter Packs

4.23.1 Filter Handling Precautions. These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme caution must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.

- Handle the filters only on the edge.
- Always wear nylon gloves when disassembling filter holders.

4.23.2 Cover work area with Kay Dry towels.

4.23.3 Place a filter cassette awaiting disassembly on one side of work area.

4.23.4 Place the prelabeled Petri slide on the work area.

4.23.5 Separate the upper section of the cassette from the lower section by inserting the filter cassette separator tool (or the back end of the tweezers) in the indentation between the two sections and prying open.

4.23.6 Push up from underneath the cassette screen to remove the screen and filter from the lower section of the cassette.

4.23.7 Using the tweezers, remove the Teflon filter from the screen. Inspect the filter and place it in its labeled Petri slide. Record any damage or unusual appearance on the field data sheet (Figure 4-12). Make sure that the magazine sequence number, if any, marked on the cassette agrees with the one on the field data sheet. Note any discrepancies on the field data sheet.

4.23.8 Store the Petri slides with the filters in a refrigerator as instructed by your supervisor.

4.23.9 Separate R&P filter cassette parts from cassette parts for other samplers. Clearly label which parts are which.

$PM_{2.5}$ Federal Reference Method (FRM) Field Data Sheet

desert research institute

SITE/SAMPLER DATA

Site Name _____

Site ID (Code) _____

Sampler Model _____

Sampler ID _____

SETUP VISIT

Date/Time _____

Technician _____

Conditions:

Indicated P_a _____ mm Hg

Indicated T_a _____ °C

Indicated Q _____ L/min

CHECK DATA (if scheduled)

P_a Standard _____

T_a Standard _____

P_a _____ mm Hg

T_a _____ °C

POST-SAMPLING VISIT

Date/Time _____

Technician _____

Conditions:

Indicated P_a _____ mm Hg

Indicated T_a _____ °C

Indicated Q _____ L/min

Reviewed by: _____ Date: _____

FIELD DATA

Filter ID	Cassette ID		Date (yymmdd)	Time (LST)	P_a (mm Hg)	T_a (°C)	Q (L/min)	Q_{avg} (L/min)	Q_{cv} (%)	V (m^3)	Comments
		Start									
		End									
		Start									
		End									
		Start									
		End									
		Start									
		End									
		Start									
		End									
		Start									
		End									
		Start									
		End									

FIELD LABORATORY

Temperature of shipping container upon arrival at Field Lab: _____ °C by: _____

Date samples shipped to DRI: _____ By: _____

Samples shipped cold: ☐Yes ☐No

Notes/comments: _____

_____

_____

DRI LABORATORY

Date pre-weighed at DRI: _____ By: _____

Date shipped from DRI: _____ By: _____

Date received at DRI: _____ By: _____

Temperature of shipping container when opened: _____ °C

Date post-weighed at DRI: _____ By: _____

Notes/comments: _____

Figure 4-12. $PM_{2.5}$ FRM field data sheet.

4.24 Cleaning and Storage of Filter Holders

4.24.1 Place mesh bags containing filter parts into the trays of the dishwasher. Make sure to keep Rupprecht & Patashnick $PM_{2.5}$ FRM filter cassette parts separate from filter cassette parts from other manufacturers.

4.24.2 Wash parts using hot water and no soap. Do not use a dry cycle or else set it to COLD.

4.24.3 Fill three plastic dishpans with DDW. Wearing gloves, rinse a bag of parts in the first, then the second.

4.24.4 Repeat for all bags, using the same dishpans in the same order.

4.24.5 Empty the bags onto the drying racks, separating the parts for faster drying. The Nuclepore bases should be laid out with the metal inlets facing up because they tend to rust and this will prevent rust accumulations on other parts

4.24.6 Store dried parts in the containers provided, either Zip-Lock bags or plasticware containers. Keep separate and clearly label Rupprecht & Patashnick $PM_{2.5}$ FRM filter cassette parts for RT filter packs.

5.0 QUANTIFICATION

(Not Applicable)

6.0 QUALITY CONTROL

(Not Applicable)

7.0 QUALITY ASSURANCE

No filters will be used before verification that the acceptance testing has been done and the filters are ready for use in the field.

All filters used will be logged out in the Filter Assignment Log Sheet (Figure 2-2).

8.0 REFERENCES

(Not Applicable)

APPENDIX A.3

DRI STANDARD OPERATING — Pages: 31
Date: 3/02
Title: Gravimetric Analysis — Number: 2-102
Revision: 5

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure provides the methods for performing gravimetric analysis of 37 and 47 mm nominal diameter polymethylpentane ring mounted Teflon membrane filters. It also covers the assignment of IDs to Teflon filters.

1.2 Measurement Principle

The Mettler Toledo MT5 Microbalance is used to weigh filters to the nearest 0.001 milligram. The separation of the weighing cell and evaluation unit ensures maximum precision – disturbing thermal influences are practically eliminated. The weighing cell and evaluation unit are interfaced together and also interfaced with a power supply unit. A weighing pan is mounted in the circular glass draft shield of the weighing cell and a glass cover is mounted on the draft shield for total enclosure. Automatic door functions on the glass draft shield facilitate operation and prevent vibrations. The Mettler Toledo MT5 Microbalance contains a fully automatic, temperature-controlled internal calibration and linearization feature which automatically calibrates the balance when necessary.

In operation, a filter is placed on the weighing pan and the door of the glass draft shield is automatically closed. After approximately 20 to 30 seconds, the filter weight is registered on the digital display of the evaluation unit.

1.3 Measurement Interferences and Their Minimization

Humidity changes affect the mass of filters and their deposits by changing the amount of absorbed water on the sample. To minimize this effect, filters are equilibrated and weighed in a temperature and humidity controlled environment (20 to 23 °C and 30% to 40% RH acceptable, 21.5 ± 2 °C and 35% ± 5% RH preferred).

Contamination from airborne particles or from particles that have accumulated on instrument and workbench surfaces is possible. Cross contamination from one sample to another is also possible. A sample can be significantly contaminated without any visible indication. The balance resides in a laminar flow hood and filters are handled only with clean tweezers to reduce the likelihood of contamination.

The microbalance is extremely sensitive to static electricity, from effects of accumulated static charge on the pan and balance beam as well as from interaction of electrically charged samples with parts of the balance. Static electrical charge on the filters, which may be significant after air is pulled through the filters during sampling, is dissipated by placing the filters over a radioactive ^{210}Po ionizing radiation source for 30 to 60 seconds prior to weighing. Static charge accumulations in the balance itself are reduced by electrically grounding the balance and periodically cleaning the weighing chamber with anti-static wipes.

Some Teflon filters exhibit a loss of weight for a period of time after they are removed from the manufacturer's containers. Weight loss of up to 150 µg has been observed. The magnitude of weight loss varies from batch to batch and may be due to loss of volatile components from the polymethylpentane support ring. New filters are removed from their sealed packages and equilibrated in a clean, open atmosphere for a sufficient time to allow the filter weights to stabilize before use (typically 3 to 6 weeks).

1.4 Ranges and Typical Values of Measurements

Unexposed filters vary considerably in mass depending on filter media and size. The 37 mm diameter filters generally weigh between 80 and 130 mg, while 47 mm diameter filters generally weigh between 110 and 160 mg.

Deposit mass depends on the air-borne particle concentration, air flow rate through the filter, sample collection time, and the particle size cut device employed. All of these factors are considered and adjusted during the development of program plans to yield optimal loading for mass measurement and subsequent chemical analyses. Most deposits range from 0 to 5 mg. Deposits greater than about 1 mg/cm^2 tend to be physically unstable.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The sensitivity of the Mettler Toledo MT5 Microbalance is 1 µg in the 0 - 250 mg range. The 0 - 25 mg range sensitivity is 0.1 µg, but this more sensitive range is not routinely used for filter measurements.

The precision of mass measurements for unsampled filters based on replicate weighings is typically 3 to 8 µg/filter. The precision on sampled filters is typically 5 to 10 µg/filter. Precision on filters with deposits heavier than 1 mg/cm^2 may approach ± 2% of the deposit mass. Deposit mass precision is the square root of the sum of the squares of the pre and post sampling precision (typically 6 - 9 µg/filter).

The lower quantifiable limit is determined as the standard deviation of field blank deposit weights. In the absence of field blanks, lower quantifiable limit can be estimated as the deposit mass precision.

Measurement accuracy is limited by the accuracy of the calibration weight and the linearity of the balance. Balance linearity is 1 µg, or 0.0001% of the load on the weighing pan. The

accuracy of the 200 mg Class 1.1 calibration weight is ±5 µg. Since deposit mass is determined by difference, the maximum error introduced from the calibration weight error is 5 µg/200 mg x 0.001 mg/µg x deposit weight (µg). In effect, accuracy is 1 µg.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand this entire standard operating procedure prior to performing filter weighing.

The laboratory manager is responsible for insuring that the weighing procedures are properly followed, maintaining the supplies necessary to insure uninterrupted weighing, and insuring proper chain-of-custody documentation.

The quality assurance (QA) officer of DRI's Division of Atmospheric Sciences has the following responsibilities: 1) to determine the extent and methods of quality assurance applied to each project; 2) to estimate the level of effort involved in the quality assurance; 3) to update this procedure periodically; and 4) to verify that the budgeted tasks are carried out as specified in each contract.

1.7 Definitions

The following terms are used in this document:

Weighing Cell	The unit of the Mettler Toledo MT5 Microbalance which encompasses the circular glass draft shield with glass cover, the weighing chamber plate and weighing pan, and the connection for the evaluation unit.
Evaluation Unit	The unit of the Mettler Toledo MT5 Microbalance which encompasses the digital display, the keypad illustrating the function keys, and the connections for the personal computer interface, weighing cell, and AC adapter.
Weighing Pan	A four prong pan, approximately 50 mm in diameter, mounted in the glass draft shield in the center of the weighing chamber plate.

1.8 Related Procedures

Sample Shipping, Receiving, and Chain-of-Custody (DRI SOP 2-209.3)
X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (DRI SOP 2-205.3)

2.0 APPARATUS, INSTRUMENTATION, AND FORMS

2.1 Apparatus and Supplies

2.1.1 Description

The Mettler Toledo MT5 Microbalance is depicted in Figures 2-1. This microbalance is designed to measure weights ranging from 0.1 μg to 3.5 grams. It resides in the Division of Atmospheric Sciences' Environmental Analysis Facility clean room, which provides a temperature and humidity controlled environment. The balance sits inside a laminar flow hood on a large block of marble providing vibration isolation.

Static charge on samples is removed using ^{210}Po ionizing radiation sources mounted inside a small plastic box (6 cm H x 7 cm W x 8 cm D). Three sources are mounted on both the top and bottom, and one on each side, all facing towards the center of the box. The front of the box is open and the back is covered with aluminum foil. Filters are placed inside the box before weighing. A ^{210}Po source in the weighing chamber minimizes accumulation of static charges in the balance as samples are processed.

The balance is connected to an Intel 86 compatible computer using the balance's built in serial interface. The Microsoft Access based program has been programmed to record sample IDs from the keyboard or barcode reader, automatically record the sample weight after a stable reading is obtained, and control movement of the balance weighing chamber doors. It records sample flags and comments entered by the operator as well as weights for initial, final, replicate and re-analysis weighings. The data ultimately reside in the Microsoft Access database, EAFDataProc.

Figure 2-1. Overview of Mettler Toledo MT5 microbalance.

Weighing Cell and Evaluation Unit

2.1.2 Characterization

The Mettler Toledo MT5 Microbalance has an average response time of 20 to 30 seconds. However, static electricity effects, humidity changes, and loss of volatile species from particle deposits may extend the time by several additional seconds. The mass reading goes directly into the database at the end of the weighing process.

2.1.3 Maintenance

Maintenance on the Mettler Toledo MT5 Microbalance consists of periodically cleaning the weighing chamber with isopropanol impregnated anti-static wipes to remove accumulated dust and static charge. Only trained personnel should perform this maintenance since the parts of the weighing chamber must be removed and special precautions must be taken to avoid damaging these parts. Compressed air should never be used to clean the chamber because dust and dirt particles may be forced into the torque motor and electronics.

The ^{210}Po source has a half life of 138 days. Change sources every six months and dispose of old sources according to manufacturer's recommendations.

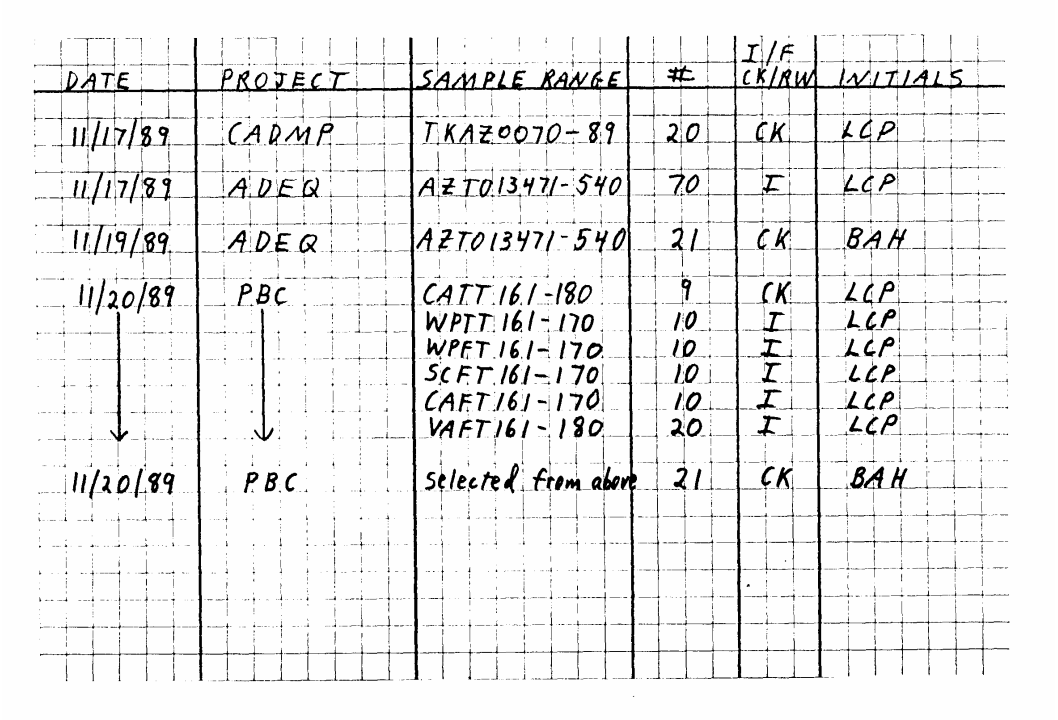
Annual cleaning and calibration and operation checks are performed by QA Services. Any additional maintenance that is required is completed at this time.

All maintenance and calibration activities are logged into the DRI Weighing Logbook (Figure 2-2).

For additional maintenance procedures, refer to the Instruction Manual for the Mettler Toledo MT5 Microbalance.

2.1.4 Parts List

- Two Class 1.1 (formerly Class M) 200 mg calibration weights , one for use as a primary standard and one for use as a working standard during routine analysis.



DATE	PROJECT	SAMPLE RANGE	#	I/F CK/RW	INITIALS
11/17/89	CARMP	TKAZ0070-89	20	CK	LCP
11/17/89	ADEQ	AZT013471-540	70	I	LCP
11/19/89	ADEQ	AZT013471-540	21	CK	BAH
11/20/89	PBC	CATT161-180	9	CK	LCP
		WPTT161-170	10	I	LCP
		WPFT161-170	10	I	LCP
		SCFT161-170	10	I	LCP
		CAFT161-170	10	I	LCP
		VAFT161-180	20	I	LCP
11/20/89	PBC	selected from above	21	CK	BAH

Figure 2-2. Example page from Filter Weighing Logbook.

- Two flat-tipped stainless steel non-serrated tweezers, one for calibration and one for routine weighing (Millipore, #62-00006).
- Teflon filters: 47 mm, 2 μm pore size (Pall, R2PJ047) and 37 mm, 2 μm pore size (Pall, R2PJ037).
- Deionizers (StaticMaster - VWR cat. no. 58580-041).
- Vinyl gloves, non-powdered (Fisher, #11-393-25).
- Kimwipes (VWR, #21905-025).
- Anti-Static Wipes (Global, #C8165).
- Glass Petri dishes, 15 mm x 150 mm (Fisher, Falcon #2045).
- Disposable Petri slides (Millipore, #PD15-047-00).
- Light table.
- Equilibration trays: two stainless steel trays hinged along one edge. Holes are drilled in the bottom tray and short rubber legs are attached to the outside of the bottom tray to provide air circulation.

- Grounding wires having alligator clips on one end to attach to the equilibration trays and banana clips on the other end to insert into a grounded electrical outlet.

- Cole-Parmer Digital Hydrometer/Thermometer (Cole-Parmer, #P-03316-66).

- Rubber bulb to blow foreign particles off of the filters (VWR, #56341-406).

2.2 Reagents

Methanol in squeeze bottle

2.3 Forms

- Filter Weighing Logbook (Figure 2-2).

- Filter Assignment Logbook (Figure 2-3).

Filter Assignment Logsheet

Cond. Date	24hr Date	Weigh Date	Proj Code	Filter Size	Box Number/ DRI Lot Number	FRM Filter Numbers	Assigned IDs (DRI Lots)

Figure 2-3. Filter Assignment Logsheet.

- Data Sheet for Filter Weight (Figure 2-4).
- Data Sheet for Replicate Weights (Figure 2-5).
- Data Sheet for Filter Re-weight (Figure 2-6).

3.0 CALIBRATION STANDARDS

3.1 Traceability of Standards

Calibration standards are 200 mg Class 1.1 calibration weights. Traceability to primary standards is maintained by the calibration weight manufacturer. An annual external calibration check makes use of standards traceable to primary standards. Two separate calibration weights are used at DRI. A reference calibration standard is used semi-annually to check the working standard. A working calibration standard is used for routine filter weighing. The weight of the working calibration standard as measured against the reference calibration standard is posted next to the balance and is used to calibrate the balance.

3.2 Use of the Standards

An internal calibration is performed on the balance at the beginning of each weighing session. The span of the balance is set with the working standard in the weighing chamber, using the working standard's most recently determined weight. The balance zero and span are set before and after each set of 10 filters are weighed.

The standards are handled only with a pair of tweezers that has been permanently labeled "CAL". These tweezers are not used for any other purpose. The working standard is kept next to the balance in a Petri dish that has been lined with aluminum foil. The reference standard is stored in a plastic vial and used only semi-annually to calibrate the working standard.

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram for this procedure is shown in Figure 4-1.

DATA SHEET FOR FILTER WEIGHT

Network Name: _____
Network Code: _____
Sampling Site: _____
Site Code: _____
Filter Type: _____
Filter Code: _____
Filter Lot No.: _____

INITIAL WEIGHT

Date: _____
Time: _____
Temp (°C): _____
Relative Humidity (%): _____
Technician: _____

FINAL WEIGHT

Date: _____
Time: _____
Temp (°C): _____
Relative Humidity (%): _____
Technician: _____

	Filter ID	Tare Weight (mg)	Initial Weight (mg)	Flag	Final Weight (mg)	Flag	Comments
	T		•		•		
	C		•		•		
1			•		•		
2			•		•		
3			•		•		
4			•		•		
5			•		•		
6			•		•		
7			•		•		
8			•		•		
9			•		•		
10			•		•		
	T		•		•		
	C		•		•		
1			•		•		
2			•		•		
3			•		•		
4			•		•		
5			•		•		
6			•		•		
7			•		•		
8			•		•		
9			•		•		
10			•		•		
	T		•		•		
	C		•		•		

Figure 2-4. Data sheet for filter weight.

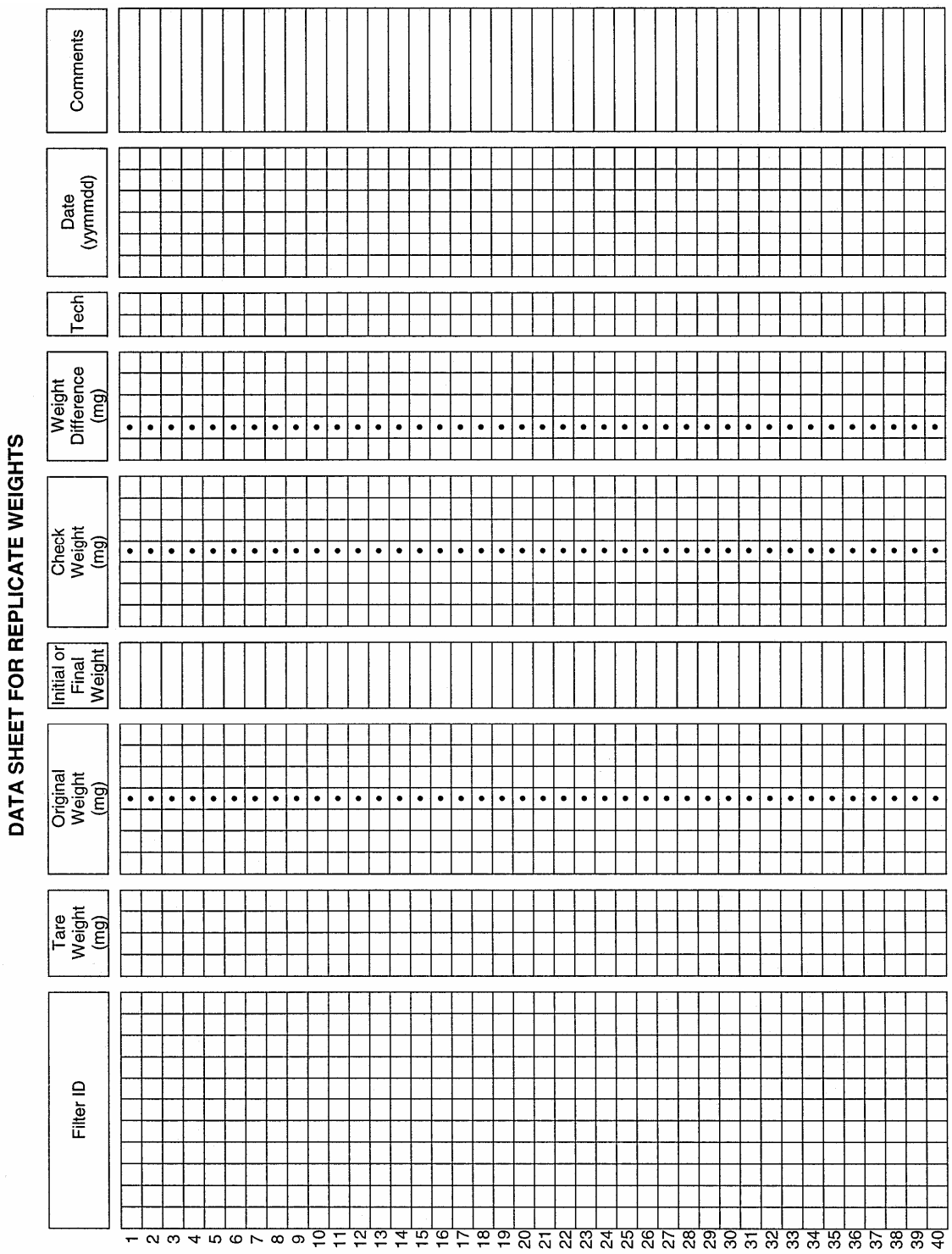


Figure 2-5. Data sheet for replicate weights.

DATA SHEET FOR FILTER REWEIGHT

Network Name: _____
Network Code: _____
Sampling Site: _____
Site Code: _____
Filter Type: _____
Filter Code: _____
Filter Lot No.: _____

INITIAL WEIGHT

Date: _____
Time: _____
Temp (°C): _____
Relative Humidity (%): _____
Technician: _____

FINAL WEIGHT

Date: _____
Time: _____
Temp (°C): _____
Relative Humidity (%): _____
Technician: _____

	Filter ID	Tare Weight (mg)	Initial Weight (mg)	Flag	Final Weight (mg)	Flag	Comments
	T		•		•		
	C		•		•		
1			•		•		
2			•		•		
3			•		•		
4			•		•		
5			•		•		
6			•		•		
7			•		•		
8			•		•		
9			•		•		
10			•		•		
	T		•		•		
	C		•		•		
1			•		•		
2			•		•		
3			•		•		
4			•		•		
5			•		•		
6			•		•		
7			•		•		
8			•		•		
9			•		•		
10			•		•		
	T		•		•		
	C		•		•		

Figure 2-6. Data sheet for filter reweight.

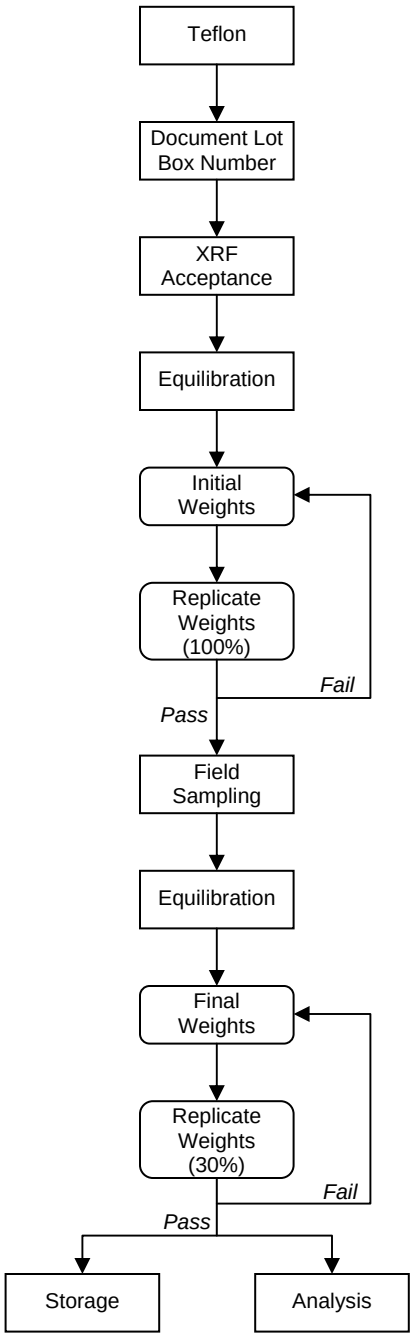


Figure 4-1. Filter weighing flow diagram.

4.2 Filter Equilibration

This section provides procedures for equilibrating pre-sampling and post-sampling filters. The pair of tweezers to be used for routine measurements should be permanently marked "FILTER" so that it is not switched with the calibration tweezers that have been marked "CAL".

4.2.1 Equilibration of Unexposed Filters

Equilibrate filters for weighing only after they pass acceptance testing by XRF. When boxes are received from the manufacturer or sponsor, one filter is removed and labeled for XRF acceptance testing. The rest of the box is kept in the weighing room until needed. Before performing initial weights, equilibrate Whatman filters for a minimum of four weeks, unless replicate weighings of lot blanks over time periods of days to weeks indicate that weight stability has already been achieved.

- Wearing gloves, clean an equilibration tray with methanol-moistened Kimwipes. Also clean a 15 mm x 150 mm glass Petri dishes for each lot. Label each dish with the manufacturer's lot/box number using a small gummed label. Be sure that all particles or fingerprints are removed from all surfaces.

- Open a box of filters that have passed XRF acceptance testing. Using the flat tipped tweezers that have been labeled for filter use, hold the filters one by one over the light table, examining each for holes or filter defects. If there are any foreign particles on the filter, remove them by blowing the surface of the filter with a rubber bulb. Filter defects include the following:
  - pinholes
  - separation of the Teflon from the support ring
  - particles that cannot be blown off with the rubber bulb
  - chaff or flashing on the ring or heat seal area that would prevent proper sealing during sampling
  - obvious discoloration that might indicate contamination
  - drastic variations in density across the surface of the Teflon membrane (Note that some variation in density of the Teflon membrane is normal; reject only those that would result in non-uniform deposits.)

- Place rejected filters into a container marked "Rejects".

- Place filters not rejected in an overlapping circular pattern in the Petri dish creating a rosette design. Place approximately 50 filters in each Petri dish. Set the full dish in the equilibration tray. Ground the equilibration tray by attaching the alligator clip to the tray and putting the jack in the ground hole of a 3 prong wall plug socket.

- Record the lot number and date of equilibration in the proper section of the Filter Assignment Logbook (Figure 2-4). The date weighed will be recorded when the filters are first used for a project. This will provide a record of the equilibration time and help determine an actual minimum equilibration time.

4.2.2 Equilibration of Exposed Filters

- Confirm that the samples have been properly logged in (DRI SOP 2-113.2).

- Equilibrate exposed filters for a minimum of 24 hours before weighing. Before proceeding, verify that the equilibration temperature and relative humidity conditions (20 to 23 °C and 30% to 40% RH acceptable, 21.5 ± 2 °C and 35% ± 5% RH preferred) were met.

- Wearing gloves, clean the work surface of the laminar flow hood (or an equilibration tray if the laminar flow hood if full) with methanol moistened Kimwipes.

- Place the Petri slides containing the exposed filters on the counter of the laminar flow hood or in the equilibration tray. Arrange them sequentially in rows of ten. This arrangement allows the technician to more easily estimate the time required for weighing a batch of filters, since the calibration checks are performed after each set of ten. Place the first row about two inches from the back of the laminar flow hood. To prevent any cross contamination; do not equilibrate or set both exposed and unexposed filters in the same area or tray.

- Open the lids and set them slightly ajar on the bottom half of the slide so that the filters can come to equilibrium with the temperature and humidity controlled air in the room. Take care that the lid is not so far ajar that it can tip and contact the filter. The Petri slides have a tweezers access opening in the front of the holder, so that the lid does not have to be opened very far.
- Post a note indicating the project, date, and time equilibrated on each set of equilibrating filters. If the filters are in a tray, the end of the tray should be labeled with the same information using a permanent marker. Do not weigh filters until 24 hours of equilibration time has elapsed and the temperature and relative humidity conditions have been satisfied.

- Close the lids of the equilibration trays, if used, and attach the grounding wires.

4.3 Routine Operation

4.3.1 General Remarks

No food is allowed in the clean room. Drinks are allowed in order to prevent dehydration and drowsiness; keep them away from the computer and do not put them inside of the laminar flow hood.

Use black ball-point pen for all recording purposes. Blue pen does not copy well. Red pen is used for validation and correction. Pencil is erasable and felt tip pens can smear so neither of these can be used when a permanent record is necessary.

Make corrections by drawing a single line through the entry and then posting the correction in the Comments column. Do not use white-out.

Do not begin weighing unless there is enough time to complete a set of ten filters and two sets of calibrations.

If the tweezers ever touch the exposed area of the filter, clean them with the anti-static wipes. Stringently avoid cross contamination.

4.3.2 Assigning IDs to Unexposed Filters

Obtain a Filter Weigh Sheet (Figure 2-5) for the project. For ongoing projects, check the weighing binder to determine if additional entries can be made to a previous sheet or if a new sheet is required.

Obtain labels for the Petri slides. The labels for ongoing projects are filed in the weighing room. Use "Bar Tender", a commercially available software program, to generate the labels for a new project.

Obtain the Filter Assignment Logbook (Figure 2-4) located to the left of the weighing platform. Record the size of the filters and corresponding IDs assigned to each DRI lot number.

Occasionally, it is necessary to reassign filters from one project to another. This occurs if the scope of work for a project changes and too many filters have already been weighed. Ideally, all reassigned filters should be re-weighed. If time does not allow this, perform the 30% replicate weighing. For reassignment without re-weighing, use the sheet with the original IDs and record new IDs next to the old in RED pen. Place the new barcode label over the top of the old in case there is any question about reassignment.

4.3.3 Weighing Unexposed Filters

Verify that filters to be weighed have been equilibrated for at least four weeks or that replicate weights of laboratory blanks over a period of days to weeks indicate stable weights before proceeding.

Wear gloves while performing all weighing procedures.

Clean the top of the balance, the marble support, and the work surface of the laminar flow hood near the balance with methanol moistened Kimwipes. Clean the deionizer box by blowing it out with the rubber bulb. Clean the CAL and FILTER tweezers with anti-static wipes.

Remove a Petri dish containing equilibrated filters from the equilibration tray and place it on the weighing platform. Assemble the Petri slides and the barcode labels that are needed.

Use the following step-by-step instructions for the Microsoft Access program to weigh filters:

- Click on the icon 'Run local'. Type in Name and Password. Choose the object Forms.

- Select Forms, WeightsDE. The weighing form will appear on the screen (Figure 4-2).

- Provide the following pertinent information:
  - Project
  - Site
  - Year
  - Equilibration Date/Time
  - Weighing Type

- Click on the Start button. At the beginning of a weighing session, a Tare and Calibration weight check will be performed. A Tare check is a weight with the weighing chamber empty and the weight should be zero. A calibration check is a weight with the standard calibration weight in the weighing chamber.

- A small box will appear with the message:
  Taring. Please empty pan OK .
  When the weighing chamber is empty, click on the OK button. The weighing chamber will close and the weighing process will begin. At the end of the tare weighing a beep will sound. Enter the tare weight on the weighing sheet (Figure 2-5).

- After the tare weighing is completed, a small box will appear with the message:

  Calibrating. Please place 200 mg calibration standard on pan OK

  Place the standard calibration weight in the weighing chamber with the CAL tweezers and then click on the OK button. The weighing process will start again. If the calibration weight is within specification, a beep will sound. Enter the calibration weight on the weighing sheet (Figure 2-5). Return the calibration standard to it's container. If the calibration weight is not within specification, a message will appear which reads:

  The 200 mg standard precision has been exceeded. Please tare and calibrate (Tare/Cal) again and reweigh the last 10 filters OK

  Click on OK. Notice that the Start button has changed to a Tare/Cal button. The Start button exists only at the beginning of the weighing session. Click on the Tare/Cal button and prepare to perform a beginning Tare (T) and Calibration (C) check again. Enter the calibration weight on the weighing sheet (Figure 2-5). Return the calibration standard to it's container. Now the weighing process for the filters is ready to begin.

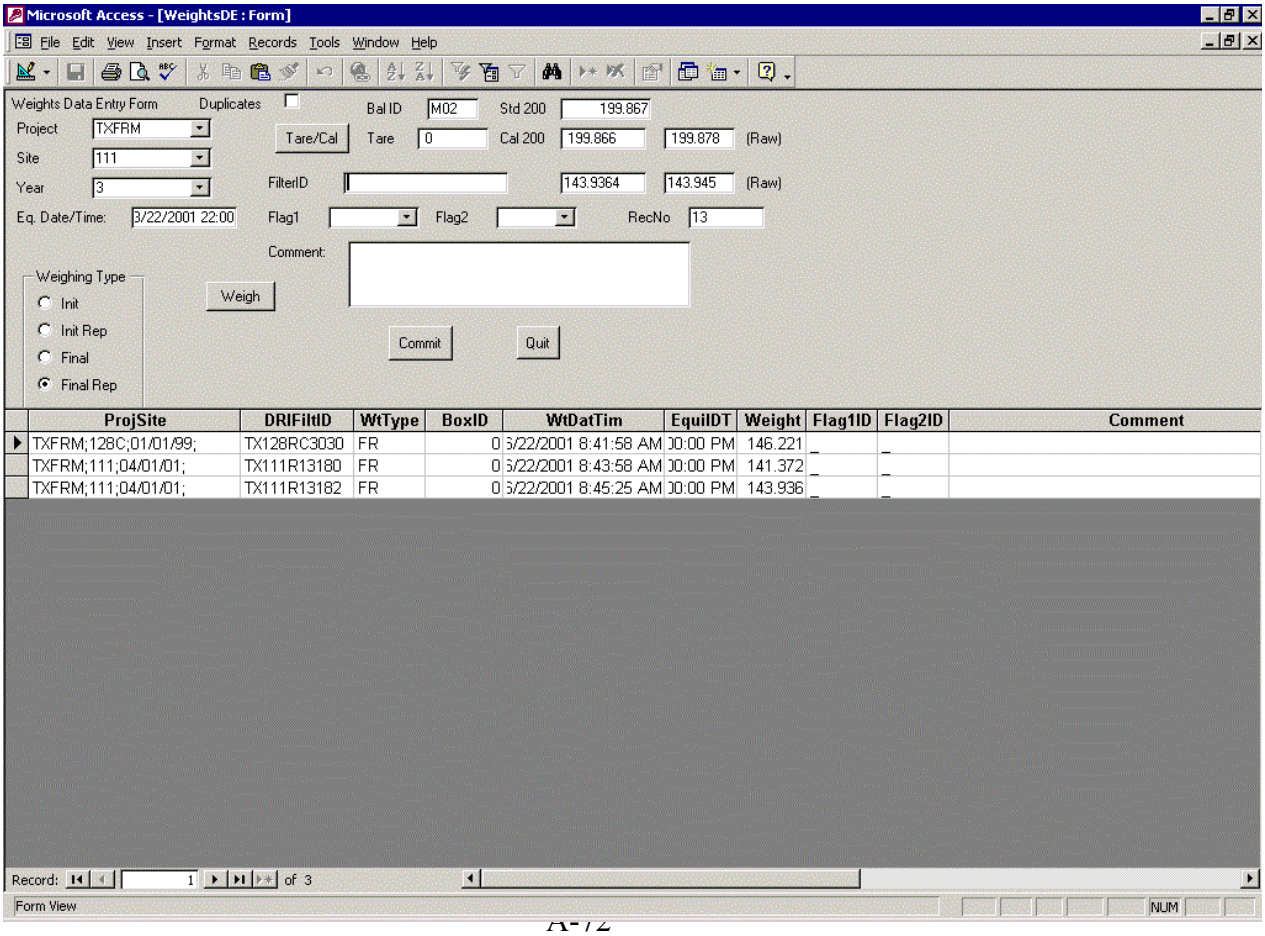


Figure 4-2. Microsoft Access data entry screen for filter weighing.

- While the calibration weight is being weighed, remove a filter from the glass Petri dish and put it in the deionizer box. Put a Petri slide with a barcode label on it in front of the box.

- While the calibration weighing is proceeding, also fill out the top section of the weighing sheet (Figure 2-5) with the required project and filter media information. Record data, time, humidity, temperature, and technician information in the Initial Weight section.

- If there is unusual instability or if the T and C values seem unusually high, it is likely that the weighing chamber has particulate matter suspended in it. Notify the supervisor who will clean the weighing chamber using the following procedure. Carefully remove the glass top of the weighing chamber. Carefully remove the pan with tweezers and place the pan on the Kimwipe. Clean inside of the weighing chamber with an anti-static wipe. Do not use compressed air in the chamber because particles could be forced into the torque mechanism. Using the rubber bulb, blow gently on the weighing pan to remove dust. Carefully replace the pan and the glass top of the weighing chamber using the same technique.

- Move the filter from the deionizing box and place it on the sample pan, centering it carefully. Scan the barcode label attached to the slide. Verify that the ID displayed on the computer screen is the correct ID. If it is not, click on the window where the ID appears and rescan the ID with the barcode reader. If the barcode is not scanned correctly, manually enter the ID in the window labeled 'FilterID'. Place the slide corresponding to this filter in front of the weighing chamber.

- Place the next filter into the deionizer box. Put its corresponding slide in front of the chamber. By having only two slides and two filters on the weighing platform, there will be little chance of switching filters.

- Click on WEIGH. This will automatically close the weighing chamber door. During the weighing process, record the first 3 digits of the filter weight on the Filter Weigh Sheet. At the end of the weighing process, which is about 20 seconds, record the last 3 digits of the weight. The manual entry of the mass is meant to be a check on the computer determination. DO NOT simply copy the digits from the screen display.

- Remove the filter and put it in the prepared slide and place the slide in the laminar flow hood. Leave the lid ajar, proceed to the next filter, and arrange the weighed filters in rows of ten for replicate weighing.

- Periodically check both the temperature and relative humidity. If the temperature has changed by more than a few tenths of a degree Centigrade or the relative humidity has changed by about 1% RH or more, enter the new value(s) onto the weight sheet.

- Tare and calibration checks are performed after each set of ten samples. The Microsoft Access weight form, WeightsDE, will automatically prompt for a Tare and Calibration check as it did at the beginning of the weighing session. Post the values in the "T" or "C" row on the weighing sheet. If the calibration weight differs by more than ± 0.005 mg from it's true value, the previous set of ten filters must be re-weighed after re-taring and recalibration. See Section 6.2 for the re-weighing procedure.

- As each filter or T and C weight are weighed, the weight information is displayed in the lower half of the WeightsDE form. See figure 4-2. After a set of 10 filters have been weighed and shown in the lower half of the form, click on Commit . This will save the weight data into the Access database, EAFdataProc. If this step is not taken and the user quit from the form at the completion of the weighing session, the weight data would not be in the database and the user would have to reweigh the filters.

- Click on Quit to exit the form at the completion of the weighing session.

4.3.4 Weighing Exposed Filters

Follow the cleaning, project directory access, recording and calibrating procedures described in Section 4.3.3, and then proceed with the following instructions:

- While the machine is weighing the calibration standard, open the Petri slide containing the first exposed filter to be weighed. Take care that any static electricity that may have built up in the slide does not cause the filter to jump out. Examine the filter. If there is anything strange about the deposit or the appearance of the filter, note it on the weighing sheet with the correct flag(s)

and/or comments columns (see Section 6.3). Any loose foreign particles should be removed by using the rubber bulb or tweezers. Do not blow on resuspension samples, however, because the deposits are not well fixed on the filter. After the visual examination, place the filter in the deionization box.

- When the tare and calibration are completed, the exposed filters can be weighed. Remove the filter from the deionization box and place it on the sample pan, being careful to center it. Scan the barcode label attached to the slide. Verify that the ID displayed on the computer screen is the correct ID. If it is not, click on the window where the ID appears and rescan the ID with the barcode reader. If the barcode is not scanned correctly, manually enter the ID in the window labeled 'FilterID'. Place the slide corresponding to this filter in front of the weighing chamber.

- Place the next filter into the deionizer box. Put its corresponding slide in front of the chamber. By having only two slides and two filters on the weighing platform, there will be little chance of switching filters.

- Prior to the weighing process, enter analysis flags that may apply to the exposed filter in the windows labeled 'Flag1' and/or 'Flag2'. There are drop down windows for these categories which list the all the appropriate flags. If there are any comments not covered by the flag (e.g., the location of a hole or scrape, whether or not a particle was removed before weighing, etc.), enter these in the window labeled 'Comment'. Now begin the weighing process.

- Click on WEIGH. This will automatically close the weighing chamber door. During the weighing process, record the first 3 digits of the filter weight on the Filter Weigh Sheet. At the end of the weighing process, which is about 20 seconds, record the last 3 digits of the weight. The manual entry of the mass is meant to be a check on the computer determination. DO NOT simply copy the digits from the screen display.

- Periodically check both the temperature and relative humidity. If the temperature has changed by more than a few tenths of a degree Centigrade or the relative humidity has changed by about 1% RH or more, enter the new value(s) onto the weight sheet.

- Tare and calibration checks are performed after each set of ten samples. Post the values in the "T" or "C" row on the weighing sheet. If the tare is not zero, the program will prompt the user to retare immediately. The tare will always be zero prior to the calibration. If the calibration value is within ±0.005 mg, proceed to weigh the next set of filters. If the calibration weight differs by more than ± 0.005 mg from it's true value, than the previous set of ten filters must be re-weighed after re-taring and recalibration. See Section 6.2 for the re-weighing procedure.

- As each filter or T and C weight are weighed, the weight information is displayed in the lower half of the WeightsDE form. See figure 4-2. After a set of 10 filters have been weighed and shown in the lower half of the form, click on Commit . This will save the weight data into the Access database, EAFdataProc. If this step is not taken and the user quit from the form at the completion of the weighing session, the weight data would not be in the database and the user would have to reweigh the filters.

- Click on Quit to exit the form at the completion of the weighing session.

- After weighing, the filters are returned to the equilibration area with the lids ajar, awaiting replicate testing (see Section 6).

4.3.5 Replicate Weighing and Re-weight Weighing

Replicate initial and final weights are collected by a second technician according to the following procedure:

- Wearing gloves, tare and calibrate the machine as described in Section 4.3.3.

- For replicate initial weights, reweigh all ten filters in each set of ten weighed filters. For replicate final weights, select three filters at random from each set of ten weighed filters.

- Turn to the Replicate Weigh Sheet (Figure 2-6) which is on the back of the Weigh Sheet and record the first selected filter ID in the first column. Note whether the weights measured are initial or final replicates in the fourth column.

- Weigh the filters as described in Section 4.3. Record the weights in the column marked Check Weight. Record the original and net weights in the appropriate columns. Fill in the technician and date columns.

- In the case of initial weights, if the ten replicate weights are within ± 0.010 mg, the set of ten has passed; mark “OK” in the “Comments” column. In the case of final weights, if the three replicate weights are within ± 0.015 mg, the set of ten has passed; mark "OK" in the “Comments” column.

- If the replicate weights are outside of the appropriate criteria, the corresponding set of ten filters must be re-weighed. Cross out the initial weights with two diagonal lines, forming an X through the data, but not obliterating it. Obtain a Reweigh Sheet (Figure 2-7) and staple it to the back of the Weigh and Replicate Weigh Sheet. Reweigh the set of ten, making sure that the new values are recorded in the same area of the reweigh sheet as on the original weight sheet.

Place them in the hood, with the lids ajar, for replicate weights. Be sure that the headings of the form are completed because these re-weights become the active weights and will replace the original weights when they are stored in the access database, EAFdataProc.

- Notify the Laboratory Supervisor that there were samples to be re-weighed and that another replicate weighing is required.

- When unexposed filters are being weighed, if there is a consistent negative replication (> 0.010 mg), it is usually a sign that the filters have not equilibrated long enough. In this case, notify the Laboratory Supervisor.

- If the set has passed, replace the container lids, being careful not to bend or tear the filters. Put these filters in a tray marked with the project and the ID range and place them in the designated storage area

- Record all activities in the DRI Weighing Logbook.

4.4 Shut-Down

After weighing is completed, click on Quit to exit the Access from, WeightsDE.
Be sure that all maintenance activities and weighing activities are recorded in the proper books.

File the weight sheets in alphabetical order according to project name in the appropriate binders located in the weight room.

4.5 Abbreviated Checklist

- Equilibration of unexposed filters

  — Verify acceptance testing results.
  — Clean equilibration trays and large glass Petri dishes.
  — Label Petri dishes.
  — Light check and arrange filters in Petri dishes.
  — Place in equilibration trays.
  — Attach alligator clips.
  — Label tray with filter size and date of equilibration.
  — Record information in the Filter Assignment Logbook.

- Routine Weighing

  — Clean area.

- Use the Microsoft Access form, WeightsDE, to access the correct mass weighing database entry form.
- Obtain weighing sheet.
- Indicate 'Weighing Type' on WeightsDE form to select option for initial, final, or replicate weighing (see Figure 4-2).
- Replicate weighing performed by another technician.
- On WeightsDE from, Commit data to database.
- Record information in the proper logbooks.

5.0 QUANTIFICATION

5.1 Calibration Procedures

Routine calibration checks are performed before and after each set of ten filters as described in Section 4.3.

The working calibration standard is checked against a second Class 1.1 primary calibration standard every six months by the Laboratory Supervisor. This check consists of ten replicate weighings of the working standard after the balance is calibrated against the primary standard using a calibration value of 200.000 mg. The average and standard deviation of these multiple weighings are calculated, and the posted calibration value is updated if necessary. It is best to perform the calibration check procedure after a project has ended and before a new one begins, since the validation procedures (see Section 5.2) would be affected by the difference in the calibration weight.

5.2 Calculations

The weights are integrated into the Access database, EAFDataProc, through the use of form WeightsDE. See DRI SOP 3-004, "$PM_{2.5}$ FRM Data processing and Data Validation", for further details.

6.0 QUALITY CONTROL

6.1 Performance Testing

Field blanks are normally supplied and collected at the rate of about 10% or more of the total number of samples for each project or network site. The actual frequency may vary somewhat depending on the shipping schedule and frequency of sampling at a given site. In addition, some networks may use field blanks as emergency spare filters. Field blanks are weighed to provide background levels present in the field during sampling and check for potential contamination during transport and handling.

Laboratory blanks are weighed and retained at the rate of 2% of the total number of filters assigned to a given project. Filter IDs xxxx050 and xxxx100 are kept for non-dichot sampling and xxxx049, xxxx050, xxxx099 and xxxx100 for dichotomous sampling. The reason for keeping more dichotomous filters is so that the even/odd numbering/sampling sequence integrity is maintained. Laboratory blanks are removed from storage and weighed when the range of samples returned includes the archived filter IDs. The use of lab blanks provides a measure of filter mass stability, uniformity of weighing room conditions, and weighing room cleanliness. While weighing laboratory blanks, the technician should calculate the difference between the initial and final weights. If the resulting lab blank weights are >± 0.015mg, the supervisor should be notified.

6.2 Reproducibility Testing

Replicate weighings are performed on 100% of the filters weighed before sampling (initial weights or pre-weights), and on 30% of the filters weighed after sampling (final weights or post-weights).

Replicate pre-sampling (initial) weights must be within ± 0.010 mg of the original weights. Replicate post-sampling (final) weights on ambient samples must be within ± 0.015 mg; post-sampling weights on heavily loaded (i.e., greater than 1 mg) samples must be within 2% of the net weight.

6.3 Control Charts

All calibration (zero and span) and replicate data points are checked. If any measurement is not within specified limits, samples are re-weighed as described in Section 4.3. Similarly, 24-hour and current temperature and humidity conditions are checked prior to starting weighing procedures. Control charts are produced from data in the Access database to periodically document the weighing room conditions.

Control charts are prepared daily for 24-hour mean and maximum values for weighing room temperature and relative humidity as shown in Figure 6-1.

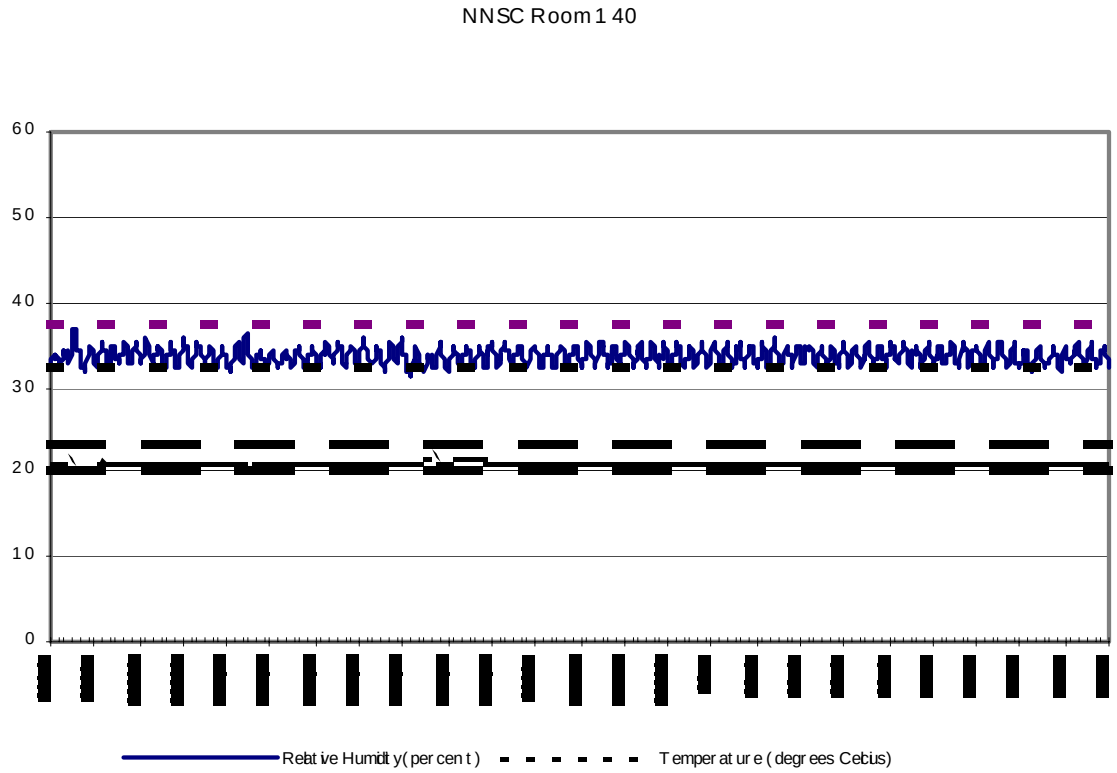


Figure 6-1. Example of chart for weighing room temperature and relative humidity control.

6.4 Flags for Non-Standard Procedures

The technician should record any unusual deposit appearances or filter damage in the comments sections of the weigh sheets and the Microsoft Access WeightsDE form. Flags are applied during weighing and follow the current DRI analysis flags definitions.

The most commonly used flags are:

b1	field blank
b2	laboratory blank
f2	filter damaged, inside analysis area*
f3	Teflon membrane substrate separated from the support ring
f4	filter loaded in Petri slide deposit side down
f5	filter dropped during handling
f6	filter stuck to Petri slide
i1	inhomogeneous filter deposit
i2	deposit smeared or scraped after sampling*
i3	deposit appears to have fallen off

i4	foreign particles on the filter*
i6	particles larger than the inlet device allows
i8	deposit on back of filter
w1	pre-weight is questionable
w2	post-weight is questionable

When the flags with an asterisk (*) are applied, an explanation of the damage or particle type should be made in the comments section as well as whether or not the particles were successfully removed.

A complete list of validation flags can be found in EAFMAIN X:\EafDataProc\Flags\ under the filenames FRMChemFlags.doc and FRMFldFlags.doc.

6.5 Validation

After the project file is created (Section 5.2), it must be validated. Check all mass concentrations and verify any large outliers by using the computer printouts and written data. If the data is verified and there is still a large outlier, check for possible switches of filters or use of replacement filters. Discuss any changes with the Laboratory Supervisor before taking action. It may be necessary to reweigh the filter. If the filter is re-weighed, use the proper validation flag to indicate whether the weight has changed. (See Section 6.4). If all attempts at reconciling the data fail, the mass data is flagged suspect and all supporting evidence is listed and given to the Project Manager. Supporting evidence includes, but is not limited to, re-weights, damage to the filter, foreign particles on the filter, or evidence of air leaks. Final disposition of the data will be made in Level II Validation. See DRI SOP 3-004, "$PM_{2.5}$ FRM Data processing and Data Validation", for further details.

7.0 REFERENCES

"Operating Instructions METTLER TOLEDO MT/UMT balances", Mettler-Toledo GmbH, Laboratory & Weighing Technologies, Internet: http://www.mt.com, Switzerland, 1998.

APPENDIX A.4

DRI STANDARD OPERATING PROCEDURE — Pages: 111

Date: 9/22/90

Title: X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples — Number: 2-205.2

Revision: 2

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This standard operating procedure is intended to:

- provide a basic understanding of the principles of X-Ray Fluorescence (XRF) analysis;
- to describe a method for the determination of elemental concentrations from ambient and source aerosol filter samples using the Kevex 0700/8000 XRF analyzer;
- to detail the concerns and procedures which will insure a state-of-the-art XRF analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute.

1.2 Measurement Principle

Analysis of aerosol filter samples using the Kevex 0700/8000 XRF analyzer is based on energy dispersive x-ray fluorescence of elemental components in a thin film sample. The emissions of x-ray photons from the sample are integrated over time and yield quantitative measurements of 38 elements ranging from aluminum (Al) through uranium (U) and semi-quantitative measurements of sodium (Na) and magnesium (Mg). A spectrum of X-ray counts versus photon energy is acquired and displayed during analysis, with individual peak energies corresponding to each element and peak areas corresponding to elemental concentrations. The advantages of XRF analysis include high sensitivity for a number of elements, the ability to analyze small quantities of sample, and the non-destructive nature of the analysis. In addition, because x-ray fluorescence depends on the quantum absorption and emission of photons at the M, L, and K orbitals, the technique is insensitive to the chemical state of the elements. Disadvantages include the need for a thin film sample, restrictions of filter sizes between 37 and 47 mm, and the subjection of the sample to a vacuum, resulting in loss of some volatile species such as hydrocarbons, ammonia, nitrate, chlorine, and bromine.

The source of x-rays in the Kevex analyzer is a side window x-ray tube with a rhodium (Rh) anode. These x-rays may be focused directly on the sample or modified using filters and collimators. X-rays may also be focused on one of 6 secondary targets which in turn emit x-rays used to excite a sample. X-rays from a secondary target or the tube are absorbed by the sample, exciting electrons to high level orbitals. As the electrons return to their ground state, photons are emitted which are characteristic of the quantum level jumps made by the electron; the energy of the emitted photons are, therefore, characteristic of the

elements contained in the sample. The fluoresced photons are detected in a solid state lithium-drifted silicon detector. Each photon that enters the detector generates an electrical charge whose magnitude is proportional to the photon's energy. The electrical signals from the detector are sorted into energy channels, counted, and displayed. A sample spectrum consists of characteristic peaks superimposed on a background caused by the scatter of x-rays from the tube into the detector. Spectra are collected for a specified length of time and stored on disk for later processing.

DRI uses five different analysis conditions during a single analysis run to maximize sensitivity to the full range of elements reported. Each of the analysis conditions, which correspond to different secondary targets; primary x-ray filters, x-ray tube voltage and current, and energy detection range, is designed for a specific group of elements. The elements analyzed by more than one condition are used for QA purposes.

1.3 Measurement Interferences and Their Minimization

The XRF is subject to measurement uncertainties from:

- Too much deposit material. Because DRI's XRF analysis and data processing programs for aerosol samples are designed specifically for thin films, x-ray spectra are subject to distortion if unusually heavy deposits are analyzed. This is due to internal absorption of both incident and emitted x-rays within the samples. Optimum loading is ~150 $\mu g/cm^2$ (1 mg/filter for 37 mm filters and 2 mg/filter for 47 mm filters). Adjustments in filter deposit area and sampling time and flow should be made to insure deposits are within this range.

- Too little deposit material. At low concentrations counting statistics and signal noise will dominate the calculations of elemental concentrations. Adjustments in filter deposit area and sampling time and flow should be made to insure deposits are at least 15 $\mu g/cm^2$.

- Inhomogeneous deposits. The x-ray beam is focused on an area ~2 to 4 cm^2 in the center of the filter. The results are extrapolated to the entire deposit area of the filter during data processing. Therefore, the center of the filter must be representative of the entire deposit. In addition, each of the five excitation conditions uses a slightly different analysis area, and non-uniformity of the deposit will affect inter-condition comparisons of overlapping elements.

- Large particles. Absorption of both incident and emitted x-rays occurs in the presence of large particles. This particularly affects the light elements analyzed under condition 5 (Na through sulfur [S]). In addition, large particles may be enriched in certain elements and may bias results in the same matter as inhomogeneous deposits.

- Filter thickness. Increased x-ray scattering is caused by increased filter thickness, increasing in turn the spectral background and causing problems for accurate background subtraction and quantification of elements at low concentrations. Additional uncertainties are introduced if filter thickness varies considerably within a lot, again making accurate background subtractions difficult. The solutions to these problems include using filters

from a reputable manufacturer (e.g., Gelman, Whatman, Pallflex), including blanks from each manufacturing lot in the formulation of background/blank spectra, and inspecting each filter over a light table before use.

- Background contamination. Several vendors of filter media have historically had problems with contaminations of their filters, apparently due to their manufacturing or handling process. While small levels of contaminations may be corrected during blank subtraction, such contaminations rarely are at consistent levels, and uncertainties can be relatively high, particularly if the contaminants correspond to elements of interest. Using filters from reputable manufacturers and performing acceptance tests on all manufacturing lots will reduce the affect of contaminations.

- Filter types. The DRI XRF analysis and data processing procedures are primarily oriented toward Teflon membrane filters, which are analytically clean, are thin to reduce scattering, and have known pore size and particle collection efficiencies. Historically, glass or quartz fiber filters have been used for Total Suspended Particulate (TSP) or PM_{10} monitoring. These filters may be analyzed but, due to their composition, render analysis results for light elements meaningless. Since particles are trapped within the filter matrix of quartz or glass-fiber filters, x-ray absorption within the filter fibers adds additional uncertainty. In addition, blank contamination levels and variations among manufacturers and manufacturing lots can be orders of magnitude higher for glass or quartz-fiber filters than for Teflon. Recommended filters are Teflon membrane filters from Gelman.

- Damaged filters. Uncertainties in results from analyzing the damaged portion of a filter are obvious. However, the x-ray signal is heavily dependent upon distance of the filter from the x-ray tube and from the detector. If filter is damaged so as to cause sagging or puckering which changes these distances, analysis results will also be affected.

1.4 Ranges and Typical Values of Measurements

A wide range of aerosol concentrations can be measured with this method, provided adjustments to deposit area and sampling flow and time are made to insure optimum loading on the filters (~150 $\mu g/cm^2$). Filter loadings between 15 and 1000 $\mu g/cm^2$ may be used, but results for heavily loaded samples may require manual corrections during data processing and results for lightly loaded filters will have concentrations below detection limits for many elements.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The lower quantifiable limits (LQLs) of DRI's XRF analysis depend on a number of factors, including type of filter media, manufacturer of filter media, consistency of filters with respect to thickness and background contaminations, analysis counting time, analysis conditions, and element. Typical minimum detection limits for Gelman Teflon membrane filters using four different analysis protocols are presented in Table 1-1.

Precision is determined largely by the reproducibility of filter positioning within the analyzer and by the homogeneity of the filter deposit, rather than the analyzer itself. DRI specifications call for ±10% on each element or within ±3 times the analytical uncertainties, whichever is larger. The analytical uncertainties are propagated from the counting statistics of the sample and background spectra.

Accuracy is ascertained in four ways:

- Inter-laboratory comparisons with other laboratories on the same set of samples.

Table 1

X-Ray Fluorescence Air Filter Analysis Interference-Free Minimum Detectable Limits[a] Using DRI Standard Analysis Protocols

Element	Condition Number	MDL, ng/cm^2
Al	5	17
Si	5	10
P	5	5
S	5	4
Cl	4	11
K	4	5
Ca	4	5
Ti	3	3
V	3	2
Cr	3	2
Mn	3	2
Fe	3	1
Co	3	1
Ni	3	1
Cu	3	1
Zn	3	2
Ga	2	3
As	2	3
Se	2	2
Br	2	1
Rb	2	1
Sr	2	2
Y	2	2
Zr	2	3
Mo	2	5
Pd	1	11
Ag	1	12
Cd	1	12
In	1	15
Sn	1	20
Sb	1	24
Ba	1	83
La	1	95
Au	2	8
Hg	2	6
Tl	2	6
Pb	2	5
U	2	27

[a] MDL defined as 3 times the standard deviation of the blank for a filter of 1 mg/cm^2 areal density and analysis times of 100 sec. for Conditions 1, 4 and 5, and 400 sec. for Conditions 2 and 3.

- Deviation of individual elements from a smooth curve of plotted instrument response in counts per second per μg/cm^2 versus atomic number, derived from analysis of elemental thin film standards from μMatter, Inc.

- Gross counts of a multi-element thin film standard from μMatter, Inc. which is analyzed in every run.

- Analysis of NIST (National Institute of Standards and Technology), formerly National Bureau of Standards (NBS), thin film standards.

Results for four key elements in the QA standard included in each run must be within ±5% of true or the run is repeated. Accuracy of the energy calibration is ±3 eV based on the iron (Fe) and Mo peaks in a Kevex 314 stainless steel standard.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing XRF analysis, which includes system operation, actual analysis, data processing, and immediate review of the QA data as it is produced to correct system problems.

It is the responsibility of the XRF supervisor to ensure the XRF analyses procedures are properly followed, to examine and document all replicate, QA standards, calibration results, and acceptance test data, to designate samples for reanalysis, to arrange for maintenance and repair, to maintain the supplies and gases necessary to insure uninterrupted analysis, and to deliver the analysis results in dBase format to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used in this document:

Escape Peak:	An artifact of the silicon detector and appears as a low intensity peak 1.74 KeV lower than a characteristic peak.
Filter Bar:	The filter bar can be positioned between the x-ray tube and sample to provide collimation and/or transmission filtering capability.
MLK Lines:	A series of x-ray lines corresponding to electron transitions to the M, L. and K orbitals.

Secondary Target: A metal foil upon which the primary x-rays from the x-ray tube are focused. Emission of "secondary" x-rays are in turn focused on the sample to be analyzed.

1.8 Related Procedures

SOP's related to XRF analysis activities which should be reviewed in conjunction with this document are:

- DRI SOP #6-001.1 Shipping and Mailing Procedures.
- DRI SOP #6-009.1 Field and Laboratory Safety Procedures.
- Any SOP's dealing with filter handling and shipping in conjunction with the specific sampling method used.
- DRI SOP #4-001.1 Creation, Revision, Distribution, and Archiving of Standard Operating Procedures.
- The programming, maintenance, and troubleshooting manuals for the Kevex 0700/8000 system.
- The appropriate MS-DOS or PC-DOS manual for the computer used as a remote terminal.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The components of the Kevex XRF analyzer are depicted in Figures 2-1 through 2-3. The analyzer consists of three main components:

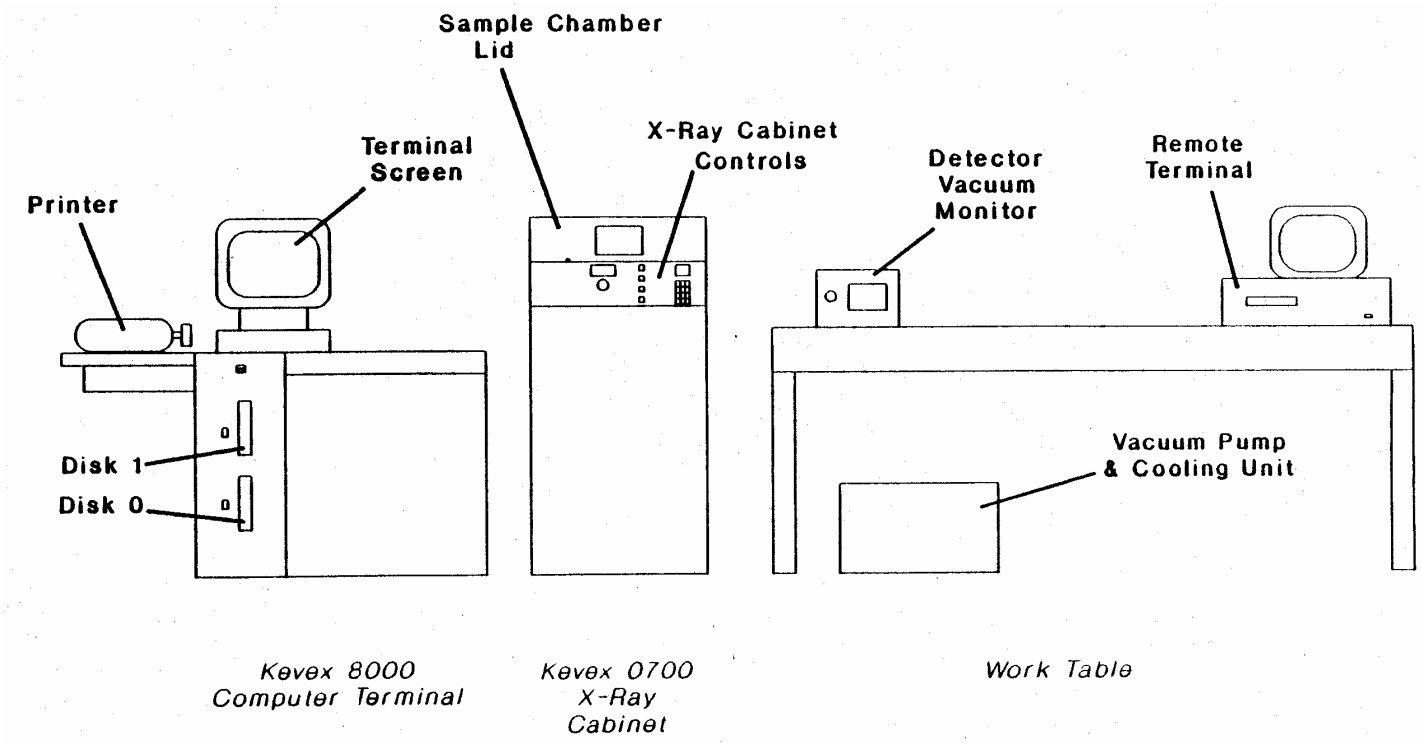


Figure 2-1. Overview of Kevex XRF Analyzer.

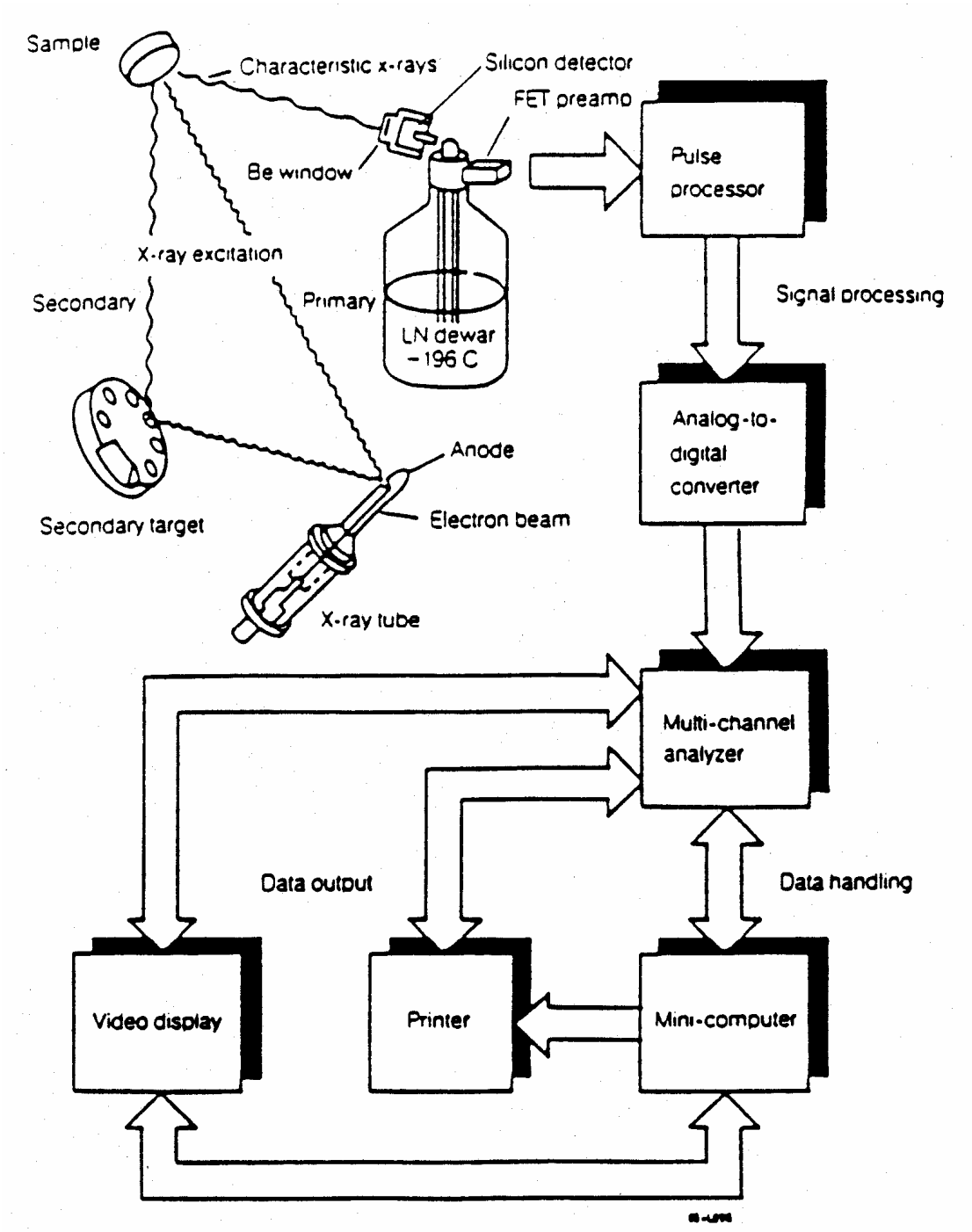


Figure 2-2. Schematic of Kevex XRF Analyzer.

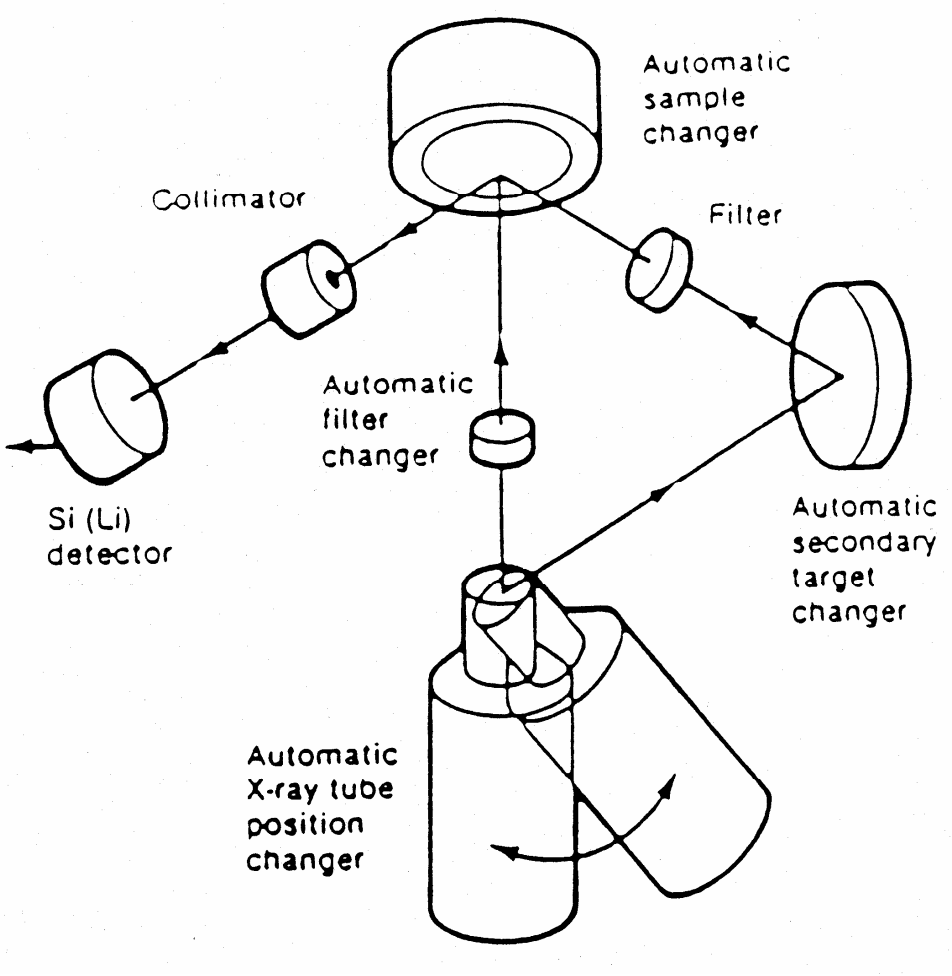


Figure 2-3. Schematic of Kevex 0700 X-Ray Cabinet.

the Kevex 0700 XRF cabinet, the Kevex 8000 computer console, and an IBM-XT as a remote terminal. Three additional support components include a vacuum pump, a detector vacuum display, and a circulating cooling unit for the x-ray tube. The following sections provide additional information on each of the three main components.

- XRF Cabinet Description

  -- The Kevex 0700 X-ray cabinet is a single enclosure for the following (see Figure 2-3):

  -- a liquid-cooled side window x-ray tube with an Rh anode rated at 60 kV and 3.3 mA. The tube is oriented vertically in the cabinet, with an output window oriented at 90° to the body of the tube. The tube's orientation is adjusted to direct x-rays through the filter bar, to the filter surface, or into the secondary target wheel.

  -- a sample carousel with 16 positions. Position #0 of this carousel is always occupied by the multi-element QA standard, for the reasons that it need not be removed between runs and that it serves to protect the detector window when the cabinet cover is open. During analysis, the sample carousel rotates to present each filter in turn to the x-ray tube/detector assembly.

  -- a cabinet cover, hinged at the back, which is opened to gain access to the sample carousel. The sample analysis area which is formed when this cover is closed is evacuated to a high vacuum during analysis to remove air molecules which would interfere with the analysis, particularly at condition 5. A thick rubber o-ring mounted on the sample chamber base provides an air-tight seal during analysis. A lead glass window and a switch for a small internal light is provided to observe the filters when the cover is closed. The cover includes a system of interlocks to prevent the operation of the x-ray tube when the cover is open.

  -- a filter bar, containing Mo and Rh foils and Whatman 41 filter paper as filters for the incoming x-rays. These filters serve to reduce the spectral background at energies below the primary excitation source energy.

  -- a wheel containing targets of germanium (Ge) and titanium (Ti). These targets allow secondary fluorescence to be used which inherently gives extremely low background for energies below the secondary target peak.

  -- a control panel (Figure 2-4), including controls for:

Vacuum on/off:	turns the vacuum pump on and off; the vacuum pump is normally left in the "on" position.
Air flow:	a three position switch, with positions for vent (to equalize the sample chamber with ambient pressure),

isolate (isolated from both ambient and the vacuum pump), and vacuum (to connect the sample chamber to the vacuum).

Display selector: a three position switch to select kV (tube voltage), mA (tube current), or μP (sample chamber pressure in μPascals).

LED display: numerical display of kV, mA, or μP, as determined by the display selector.

Reset switch: push button switch used to turn off power to the x-ray tube prior to opening the sample chamber cover.

Sample position: push button switch to allow manual input of the sample carousel position if the Mode switch is in the manual position.

Filter/Target: push button switch to allow manual input of the filter bar and secondary target wheel positions if the Mode switch is in the manual position.

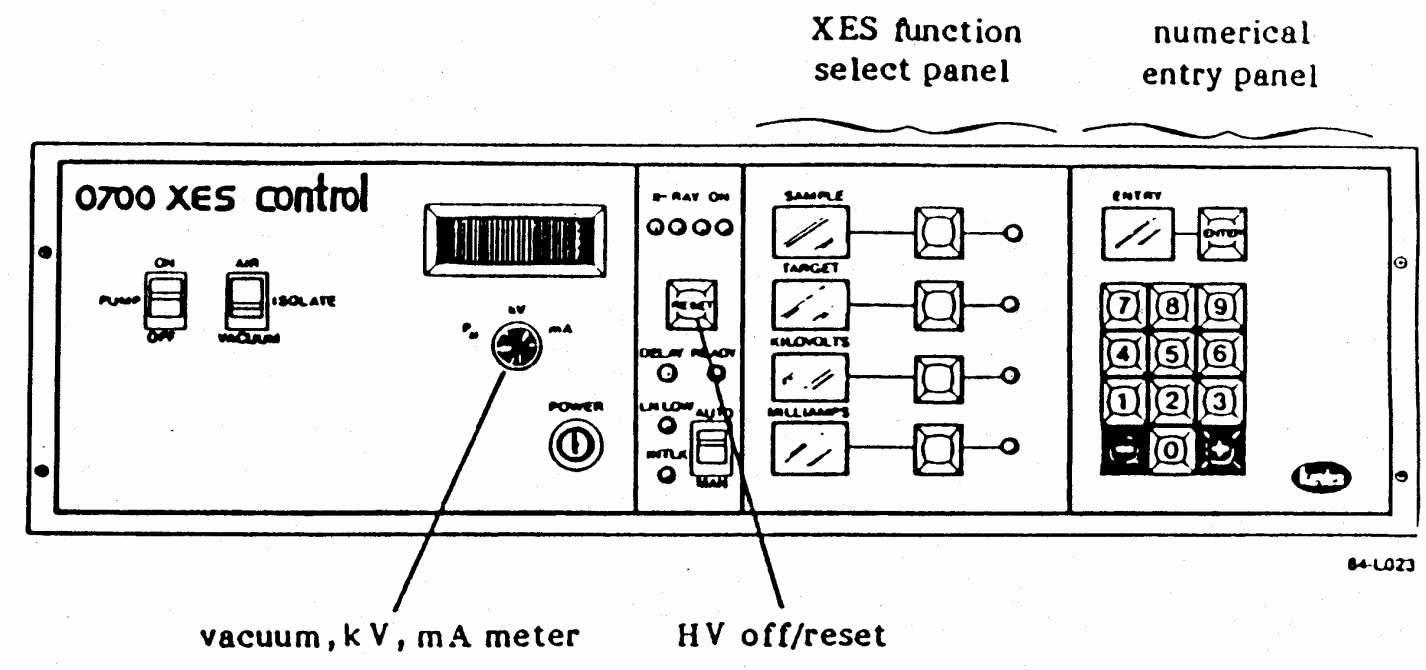


Figure 2-4 Layout of Kevex 0700 X-Ray Cabinet Control Panel .

kV button: push button switch to allow manual input of tube voltage if the Mode switch is in the manual position.

mA button: push button switch to allow manual input of tube current if the Mode switch is in the manual position.

Mode switch: two position toggle switch for selection of Auto (control by 8000 computer) or Manual (0700 front panel control) for control of carousel position, filter bar and secondary target positions, and tube voltage and current.

- Kevex 8000 Computer includes:

  -- a high-resolution color monitor, with controls for monitor brightness and speaker volume.

  -- a keyboard, which in addition to a standard QWERTY keyboard contains the following (Figure 2-5):

  0700 Controls: switches located at the top left of the keyboard which activate menus for direct control of the 0700 x-ray cabinet.

  Cursor controls: switches located at the top middle of the keyboard which allow positioning of the spectra, MLK markers, text cursor, or spectral cursor.

  KevScan control: rolling knob to control positioning of the spectra, MLK markers, or spectral cursor.

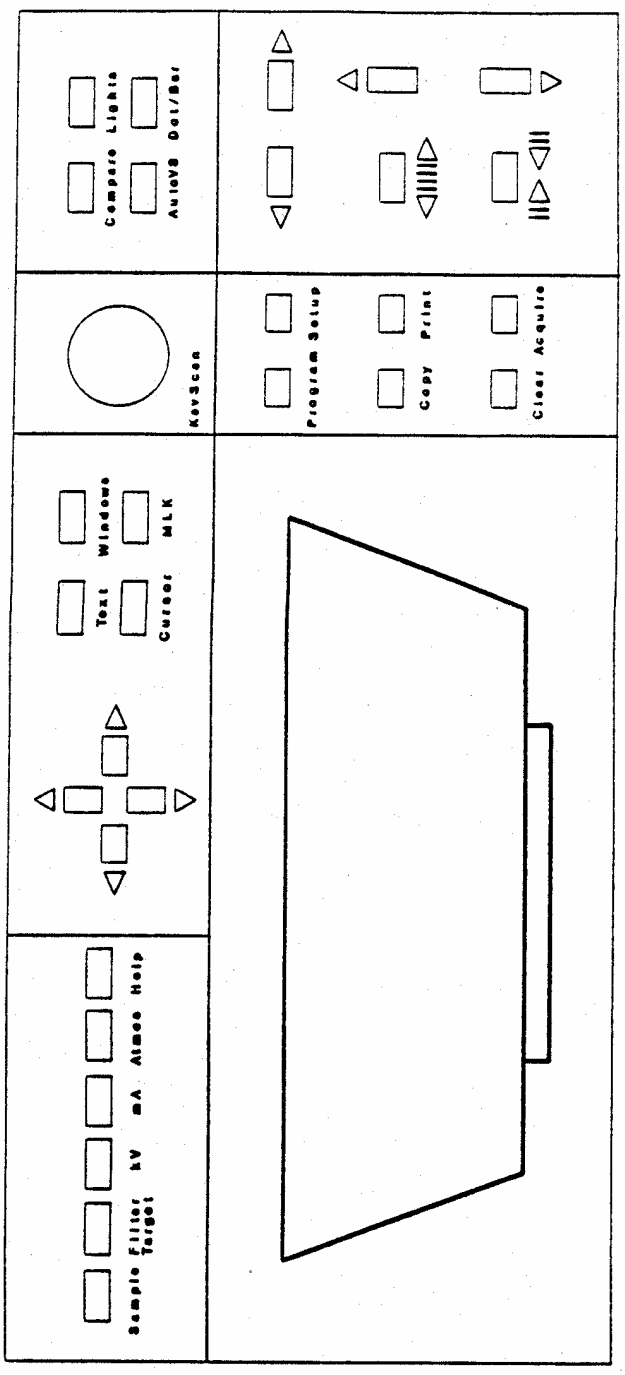


Figure 2-5. Layout of Kevex 8000 Keyboard.

Firmware switches: switches located at the immediate right of the standard keyboard which allow access to program options and contents of memory areas.

Spectrum controls: switches located at the bottom right of the keyboard which allow scaling and positioning of the displayed spectrum.

-- two 10 MB Bernoulli disk drives

-- a serial dot matrix printer

- Remote Terminal Description

  An IBM-XT with a 20 MB hard disk and one 5-1/4" double density floppy drive is connected as a second, remote terminal via an RS232 serial communications cable. This system runs a communications program called CrossTalk which emulates a VT100 video terminal. Note that this remote terminal cannot display spectra. It is used primarily for running data processing programs and capturing data to PC-compatible ASCII files for further data processing on an MS-DOS system.

- Operating System Description

  The bottom disk drive (drive 0) is reserved for the program disk. This disk contains analysis and processing programs written in Job Control Language (JCL) as well as assorted utilities. The top disk drive (drive 1) is reserved for data disks; a list of disk ID numbers for the current data disk, data backup disk, and program disk is posted in the disk storage area.

  The computer contains a LSI 11/23 processor and includes the TSX Plus operating system, which allows time-shared processing on two terminals simultaneously. The 8000 system itself comprises the first terminal which utilizes the Multi-Channel Analyzer (MCA) associated with the 0700 x-ray cabinet. The remote terminal acts as a second terminal with limited file access and utilization of a virtual MCA for spectra processing. The operating system's proprietary time-slicing algorithm has a few peculiarities, including the fact that programs running from the remote terminal will take longer to execute if the primary terminal is sitting idle.

  Because the operating system is somewhat different than DOS used on most personal computers, some explanation of the file organization and command syntax is presented here.

  The 8000 system presents three levels to the user: TSX, which is the basic operating system and is designated on the screen with a dot prompt; a utility program which allows several disk operations and loads the Kevex analysis software; and the analysis software, known as Toolbox, which is designated on the screen with an asterisk prompt. The user may shell to the TSX level from Toolbox, which allows the convenience of the basic disk operations available at that level without the necessity to reload Toolbox afterwards.

  TSX allows a number of basic disk operations, including disk formatting and file creation, copying, deleting, and renaming. File names are restricted to 6 characters with 3 character extensions; no dashes are allowed. Files visible from the TSX level that are of particular interest for filter analysis include the following:

*.U3 user-defined ASCII format, used for conversion of Toolbox *.U3 concentration results files to a form which can be transferred to the remote terminal for further processing.

*.KVX Toolbox "libraries", which have some characteristics of both subdirectories and files. Like files, they may be created, copied, renamed, and deleted. Like subdirectories, they contain a number of other files which are visible only to Toolbox.

Common commands used at the TSX level (dot prompt) are:

COPY/SETDATE FILTER.KVX DL1:xxxxxx.KVX - copies empty Toolbox library file as a template to create a new library named "xxxxxx" on the data disk in drive 1. Normally the libraries include 2 to 4 characters as a project identifier and 1 or 2 characters are used as a library number for that project (e.g., CARB12.KVX). Note that like DOS, the default drive (in this case, the source of FILTER.KVX is drive 0, the default drive) need not be specified. The SETDATE switch forces the new file to take on the current date as its creation date.

DIR *.KVX - produces a directory listing of all files with KVX extensions in the default drive (drive 0). Similarly, DIR DL1:*.KVX will produce a directory listing of the disk in drive 1. This command may be used to check for the existence of a file or to check on the amount of free space left on the disk. Note: a Toolbox library file occupies 2500 blocks.

RUN/S/IO: runs a utility program which formats the disk in drive 1. No warning is given and no other opportunity for user input is given. Use with caution. Note: this program must be followed with INIT/BAD DL1: to initialize the directory area to produce a useable disk.

INIT/BAD DL1: - runs a utility which searches for bad disk blocks; it also initializes the directory area on a newly formatted disk. This command must include the DL1: specifier to avoid erasing the directory of the program disk in drive 0. This program will not proceed unless all Toolbox logical device assignments to drive 1 are removed (reassigned to drive 0; see discussion of Toolbox below). Normally this program will return with the message "NO BAD BLOCKS DETECTED".

COPY DL1:xxxxxx.KVX - copies the "xxxxxx" library from drive 1 to the default drive (drive 0). Equivalent commands are COPY DL1:xxxxxx.KVX DL1: or COPY DL1:xxxxxx.KVX DK: (DK: is an alias for DL0:). This command is most often used during backup operations in which the library to be backed up is copied temporarily to the program disk to allow the backup disk to be exchanged with the data disk.

COPY xxxxxx.KVX DL1: - copies the "xxxxxx" library from drive 0 to drive 1 without changing its name. This command is most often used during backup operations in which the library copied temporarily to the program disk is copied to the backup disk in drive 1.

DEL xxxxxx.eee - deletes "xxxxxx.eee" file from drive 0. This command is used with the extension "KVX" when erasing a library temporarily stored on the program disk during a backup operation. It is used with "NAM" and "U3" extensions when removing temporary ASCII files during a transfer operation (see Section 5.3.3). The system always asks for confirmation of the intended deletion unless suppressed with DEL/NOQUERY xxxxxx.eee. This command will not work if the file is protected.

UNPROTECT xxxxxx.eee - removes file locking feature from the specified file to allow it to be deleted. This command is normally used in preparation for deleting a temporary library on disk 0 created during the backup operation. Note that the FILTER.KVX file used as a template for creating new libraries is locked and transfers this locked status to the new libraries; i.e., all new libraries are automatically locked and must be unlocked before they can be deleted.

TYPE xxxxxx.eee - displays the contents of an ASCII file to the screen. This command is used during the transfer operation and may include a wildcard character "*" (e.g., TYPE *.U3).

Additional commands and their syntax may be found in the TSX Plus Reference manual.

The utility which allows Toolbox to be loaded normally appears only when the 8000 computer is booted. This consists of three options on the screen, the last of which is the default option to load Toolbox. This utility may be invoked from Toolbox itself by pressing ^C (control-C).

Toolbox is the Kevex working environment which allows spectra to be collected, processed, and stored. With the exception of the TRANSFER program, it works solely within the *.KVX libraries with respect to file operations. Programs are contained within a library called PROG.KVX on the program disk in drive 0. Data are usually contained in *.KVX libraries on the data disk in drive 1, although they need not be.

Contained within the *.KVX libraries are the following file types:

NAM	name files, which contain the filter IDs in a given analysis run. The name of the name file is derived from the ID given to carousel position 0 (which is the QA standard).
SPEC	spectra files, which contain the raw spectral data as counts per channel and elapsed live time.

U2 — user-formatted file, used primarily in the form of CONSTmmddyy.U2, which contains definitions for element windows in terms of energy ranges, element names defined for reporting, and windows used for background normalization during processing of condition 5.

U3 — user-formatted file, used for containing the gross and net counts of the SPECTRA spectra processing program.

PRO — procedure files, which contain JCL commands and comprise Toolbox programs.

Note that these files are not differentiated or referenced by extensions; extensions on these files are automatically assigned by Toolbox to reflect version number and excitation condition number (if applicable).

Common commands used at the Toolbox level (asterisk prompt) are:

RUN FILTER - begins execution of the normal filter analysis program

RUN FILTER-GF - begins execution of a filter analysis program modified for glass fiber and quartz fiber filters.

RUN SPECTRA - begins execution of the spectra processing program, which removes escape peaks, performs background subtraction, and places gross and net counts in the U3 files.

RUN TRANSFER - begins execution of the file transfer program, which translates the contents of the Toolbox U3 files into TSX-11 ASCII *.U3 files.

^C (Control-C) - exits Toolbox and returns to the utility which loads Toolbox.

^A (Control-A) - interrupts the program in progress; may have to be tapped several times in a row if the program is currently in a nested routine.

The remaining common Toolbox commands are constructed using base commands followed by modifiers. In addition, Toolbox requires the use of two logical devices as references to its libraries. For example, instead of constructing a command which specifies both the command and the full description of the affected library (including both drive number and library name), a logical device assignment is made to the desired drive and library name, and all future references to that library use either 0 or 1 as an indirect reference to that library. Note that logical devices 0 and 1 have no implicit connections with drives 0 and 1; either logical device may refer to either drive. In fact, both logical devices could be set to refer to the same libraries. Normally, logical device 0 is set to the PROG.KVX library on disk 0 which contains the programs, and logical device 1 is set to the

library on the data disk in drive 1. Like the default drive (drive 0) which need not be explicitly included in a TSX command, logical device 0 need not be explicitly included in a Toolbox command.

The following are example command constructions; other permutations are intuitive:

LIB/AS 0=DL1:xxxxxx.KVX - LIBrary/ASsign logical device 0 to xxxxxx.KVX library on drive 1. All future references to logical device 0 will now reference xxxxxx.KVX in drive 1. Note that the KVX extension is optional. Also note that if reference is made to the default drive (drive 0), the drive designation is optional: i.e., LIB/AS 0=DL0:xxxxxx.KVX is equivalent to LIB/AS 0=xxxxxx.KVX.

LIB/NAM 1 - LIBrary/NAMe, logical device 1; provides a directory listing of all name files in the library referenced by logical device 1.

LIB/SPEC 1 - LIBrary/NAMe, logical device 1; provides directory listing of all spectra files in the library referenced by logical device 1. Note that this is equivalent to LIB/SPEC 1:*.*.*, using wildcards for the spectra name, version number, and condition number, respectively. More restrictive directory requests may be constructed; i.e., LIB/SPEC 1:*.1.5 will produce a directory listing of all spectra files in logical device 1 of version 1 and collected under condition 5.

PRO/COND n - PROcess/CONDition n, where n=1 to 5; prepares the system for spectra display and processing using the given condition. This has no visible effect until a spectra processing or recall command is given.

REC/SPEC 1:TESTFILE - RECall/SPECtrum, logical device 1; recalls spectrum named TESTFILE from logical device 1 for the PRO/COND currently in effect and places it on the screen for review.

REC/COMP 1:TESTFILE - RECall/COMPare, logical device 1; recall spectrum named TESTFILE from logical device 1 for the PRO/COND currently in effect and places it on the screen as dots; intended for comparison with a spectra already on the display.

TYPE/PRO FILTER - TYPE/PROcess file; enters a read-only editor mode with the contents of the PRO file named FILTER from logical device 0. Note that this is equivalent to TYPE/PRO 0:FILTER. Editor commands may be reviewed by pressing ^H (Control-H). This may also be used with U3 and NAM files by using /U3 and /NAM switches, respectively, in place of the /PRO switch.

LIB/COPY/SPEC 1:TESTFILE.*.*=TESTFILE.*.* - LIBrary/COPY/SPECtra; copies all versions and conditions of TESTFILE spectra file from logical device 0 (default device, so 0: is omitted) to logical device 1 while maintaining the same name. Note that the destination is named first. This command would be used to

transfer a set of spectra developed for background subtraction from the library were it was developed to a new library; this would be necessary before the SPECTRA program could be run on data in the new library. Note that the system will ask for operator approval before transferring each file. This may be suppressed by adding the switch /NOQUERY after SPEC.

Additional Toolbox commands may be found in the Kevex XRF Toolbox Reference manual, Version 3.2.

2.1.2 Instrument Characterization

The Kevex XRF analyzer, running under DRI's analysis programs, uses 5 different excitation conditions to maximize sensitivity to select groups of elements (Table 2-1). Four analysis protocols are available which differ only in their counting times for each of the conditions. A full analysis run of 15 samples under protocol A (the standard analysis protocol) takes approximately 7½ hours. Normally, two analysis runs per day are performed, the first started in the morning and finishing in the late afternoon, and the second started in the afternoon and allowed to run overnight.

The solid state detector is placed behind a beryllium (Be) window so as to maintain a high vacuum between the window and the detector. Be is used because it has a low enough atomic number to not interfere with the elements typically measured on this system (Na through Pb). However, the Be window is a very thin foil (0.5 mils) and is supporting a high vacuum. Because of this, the window is extremely susceptible to breakage. A number of events may cause breakage of the window, including physical shock (jarring of the x-ray cabinet or a particle from a filter falling onto the window) and chemical degradation (chemical etching by sulfur and acidic compound). Furthermore, Be is extremely toxic (Kevex Model 0700 User's Manual) and should not be inhaled or absorbed into the skin.

Therefore, the operator must take precautions at all times to prevent damage to this window. Such precautions include:

- Insuring that all large, loose particles on a filter deposit are removed before analysis.
- Placing filters with large amounts of potentially loose particles between Mylar sheets during analysis; this includes all quartz and glass fiber filters.
- Analyzing filters with high levels of sulfur or other acidic species only with the prior approval of the XRF supervisor and with the precautions he specifies, which may include placing the samples in hermetically sealed Mylar bags.
- Do not remove the QA standard in sample position 0; this sample serves to cover the window when the cabinet cover is open and affords some degree of protection to the window.

Table 2-1

Excitation Conditions of
Kevex/DRI X-Ray Fluorescence Analyzer

Parameter	Condition Number				
	1	2	3	4	5
Tube Voltage	60 KV	35 KV	30 KV	30 KV	8 KV
Tube Current	0.4 mA	3.3 mA	3.3 mA	3.3 mA	1.0 mA
Direct Mod					
Filter	Mo	Rh	None	None	Whatman 41
Thickness	0.10 mm	0.13 mm	None	None	3 layers
Secondary Target	None	None	Ge	Ti	None
Filter	None	None	Whatman 41	Mylar	None
Thickness	None	None	1 layer	3.8 μm	None
Analysis Time					
Protocol A	100 sec	400 sec	400 sec	100 sec	100 sec
Protocol B	200 sec	800 sec	800 sec	200 sec	200 sec
Protocol C	800 sec	3200 sec	3200 sec	800 sec	800 sec
Protocol D	1600 sec	6400 sec	6400 sec	1600 sec	1600 sec
Energy Range	0-40 KeV	0-20 KeV	0-10 KeV	0-10 KeV	0-10 KeV
Elements	Pd, Ag, Cd, In, Sn, Sb, Ba, La	Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Au, Hg, Tl, Pb, U	K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn	Al, Si, P, S, Cl, K, Ca	Na, Mg, Al, Si, P, S,

- Insure that the sample carousel has returned to its "home" position (sample position 0 over the detector) before lifting the cabinet cover and loading or unloading samples from the carousel.
- Under no circumstances attempt to remove particles which may have fallen on the window by physical means or by blowing on the window.
- Avoid jarring the x-ray cabinet.
- When loading samples in the carousel, do not at any time allow the filter holders to pass over the detector area when loading or unloading samples. Insure that a circuitous route is taken when placing holders in positions 10 through 15.
- Cleaning of the sample chamber or repair to the filter bar or secondary target assemblies should be attempted only by the XRF Supervisor.
- Do not open the sample chamber cover without removing all loose items such as pencils, pens, or jewelry from clothing, pocket, etc., which may fall into the carousel area.

Besides the health concerns noted above, a broken Be window requires that the entire detector and cryostat be shipped to Kevex for repair. As such, replacement times for broken windows are estimated at 3 to 6 months, and a broken window would be catastrophic for the timely analysis of samples.

The Laboratory Manager at DRI's Environmental Analysis Facility has announced a standing policy that any operator who breaks a detector window will be fired.

The operator of the XRF must be familiar with the potential health hazards of x-ray exposure. Refer to the Kevex Radiation Safety Guide and the University of Nevada Radiation Safety Manual for additional information. All operators are required to wear a clip-on film exposure badge. These badges are collected on a monthly basis and analyzed for exposure by the Radiation Detection Company. Copies of exposure reports are posted in the XRF room, and total exposure levels may be obtained from the University of Nevada System Radiation Safety Officer.

The Kevex XRF is equipped with a double interlock system to prevent operation of the x-ray tube when the sampler chamber lid is open. However, the operator should not depend on this interlock, but should check each time before the lid is opened that the x-rays are already deactivated.

The XRF detector is cooled by means of liquid nitrogen (LN2). The LN2 dewar is located in the base of the XRF cabinet and is filled on a weekly basis from a large LN2 tank stored adjacent to the XRF room. The operator must avoid skin contact with the LN2 as it is handled to avoid severe frostbite. Heavy gloves and safety goggles are provided and should be worn when filling the XRF system. In addition, a piece of cardboard should be placed over the cables at the back of the instrument during filling operations to prevent LN2 from spilling on the cables and possibly freezing and cracking the insulation.

2.1.3 Maintenance

Regular maintenance for the XRF analyzer involves:

- Weekly filling of liquid nitrogen dewar. This should be performed on Monday to allow replacement of the LN2 tank on DRI's regular gas delivery day (Tuesday) if the large LN2 tank should be empty. A plastic funnel is placed in the inlet tube at the back of the x-ray cabinet. A piece of cardboard is placed over the cables connected to the back of the instrument to protect them from spilled LN2. Wearing gloves and safety goggles, fill the small transport dewar to ¼" from the top from the large LN2 tank; this represents 4 liters of LN2. Slowly pore the LN2 into the funnel, taking care to add LN2 no faster than the funnel can accept it. NOTE: when the funnel and inlet tubing are warm, the LN2 will boil vigorously; avoid adding LN2 too fast until the funnel and inlet tubing reach LN2 temperature. Continue filling the XRF with the small transport dewar until LN2 begins to spit from the exhaust tube. Record the date, initials, and amount of LN2 added to the XRF Maintenance Logbook. NOTE: the funnel must be removed before the sample chamber lid can be opened. Wait at least 30 minutes before beginning an XRF analysis run.

- Weekly cleaning of both disk drives. Both disk drives are cleaned at the same time LN2 is added to the system. The disk drive cleaning materials are kept on the disk storage shelf in the XRF room. Remove disks from both drives. Push the cover on the drive cleaning disk until the cleaning pad is exposed. The cleaning pad is replaced every 4 or 5 weeks. Spray a small amount of cleaning solvent evenly over the pad. Slide the cover back and place the cleaning disk in drive 0. Move the small level on the end of the cleaning disk up and down 30 times to move the cleaning pad over the drive heads. Remove the cleaning disk and repeat the process for drive 1. Mark the date on the cleaning disk label and return the disk cleaning supplies to the shelf. Record the date and cleaning operation in the XRF Maintenance Logbook.

- Monthly cleaning of sample chamber or as needed. This will be performed by the XRF supervisor only! The detector window is extremely fragile and susceptible to breakage; see Section 2.1.2.

- Weekly checking level of vacuum pump oil.

- Yearly replacing of vacuum pump oil. Analysis of samples that degas or have high moisture content may require more frequent vacuum pup oil changes. If a significant amount of smoke is generated when the sample chamber is evacuated, the pump oil needs to be changed.

- Weekly checking level of antifreeze coolant.

- Yearly replacing of antifreeze coolant.

- Yearly replacing of HEPA air filter on Bernoulli disk drives.

- Weekly wiping of accumulated dust from monitor screens, keyboards, and front of x-ray cabinet.

- Checking of printer paper supply and ribbon quality before each run.

2.1.4 Spare Parts and Supplies

It is essential that the following spare parts and supplies be kept on hand to insure minimal interruptions in analysis:

- Disk cleaning kit, including felt pads and disk drive head cleaner solution (IOmega #S010013).
- 10 MB Bernoulli disks (IOmega #S010031 or equivalent).
- Mylar sheets, 2 X 2" precut squares, 3.6 μm thickness (Somar Spectrofilm, #3615-33).
- Bulk sample analysis cups, retainer guides, and retainer rings, 31 mm (Spex Industries, #3561 and #3571).
- Tweezers for handling filters (Millipore flat tipped stainless steel tweezers, #62-000067).
- Kimwipes, large (VWR, #34255) and small (VWR, #34155).
- Vacuum pump oil (Alcatel 100).
- Ethylene glycol antifreeze for use in the x-ray tube cooling system (Pep Boys automotive coolant or equivalent)
- Spare air filters for Bernoulli disk drives (Iomega #00441500).
- Copies of current "XRF Analysis Logsheet".
- Printer paper.
- Printer ribbons.

2.2 Reagents

The chemicals required for XRF analysis are:

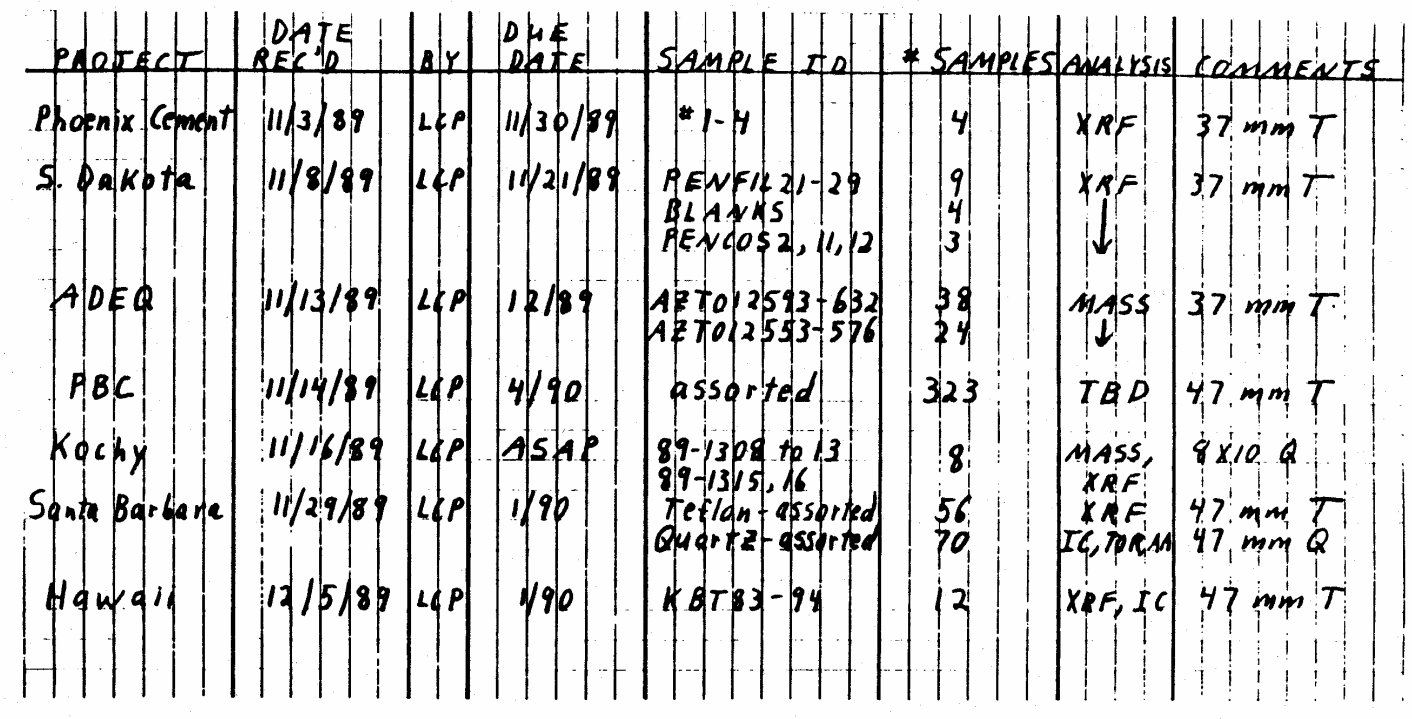
- methanol in a squeeze bottle for cleaning the sample holders and the filter loading area

2.3 Forms and Paperwork

All samples are logged into the Air Analysis Logbook upon receipt at the laboratory. Refer to Figure 2-6 for the format of this logbook. A sample analysis list will be prepared by the laboratory or XRF supervisor indicating which samples will be analyzed and any special instructions (Figure 2-7).

Samples designated for XRF analysis are logged into the XRF Analysis Logbook prior to analysis; Figure 2-8 provides an example of entries in this logbook. As each set of filters corresponding to an analysis run are loaded, the run number, load date, and technician's initials are noted in the appropriate columns.

An XRF Analysis Logsheet is completed prior to loading the samples into the filter holders. Figure 2-9 provides an example of a completed logsheet.



PROJECT	DATE REC'D	BY	DUE DATE	SAMPLE ID	# SAMPLES	ANALYSIS	COMMENTS
Phoenix Cement	11/3/89	LCP	11/30/89	*1-4	4	XRF	37 mm T
S. Dakota	11/8/89	LCP	11/21/89	RENFIL21-29	9	XRF	37 mm T
				BLANKS	4	↓	
				RENCOS2, 11, 12	3		
ADEQ	11/13/89	LCP	12/89	AZT012593-632	38	MASS	37 mm T
				AZT012553-576	24	↓	
PBC	11/14/89	LCP	4/90	assorted	323	TBD	47 mm T
Kochy	11/16/89	LCP	ASAP	89-1308 to 13	8	MASS, XRF	8X10 Q
Santa Barbara	11/29/89	LCP	1/90	89-1315, 16			
				Teflan-assorted	56	XRF	47 mm T
				Quartz-assorted	70	IC, TOR/M	47 mm Q
Hawaii	12/5/89	LCP	1/90	KBT83-94	12	XRF, IC	47 mm T

Figure 2-6. Format of the Air Analysis Logbook.

Santa Barbara Teflon Filters: XRF

Date: 8/22/89
From: L.Pritchett
To : J.Chow
J.Watson
C.Frazier
XRF Room

Total number of samples: 52

Species to be analyzed:
elements: by XRF

Instructions:

1. This list includes the filters designated for analysis from the third quarter of sampling for the Santa Barbara project. These are filters from only the first half of the third quarter.

2. XRF analysis will start Thursday, 8/24/89. Analysis will be using Protocol A. Run ID will start with SABA-17, in library SABA6.KVX.

3. Deposit area for these filters is 13.8 cm2.

4. dBase III files will be named:

XRF data : SAEL03A.DBF

Filter	Description	XRF
SATB13	Lab blank	Y ____
SATB14	Lab blank	Y ____
SATB15	Lab blank	Y ____
SATB17	Lab blank	Y ____
AT6027	Ambient	Y ____
AT6028	Ambient	Y ____
AT6029	Ambient	Y ____
AT6030	Ambient	Y ____
AT6031	Ambient	Y ____
AT6032	Ambient	Y ____
AT6033	Ambient	Y ____
AT6034	Ambient	Y ____
BT1043	Ambient	Y ____

Figure 2-7. Example of XRF Sample Analysis List.

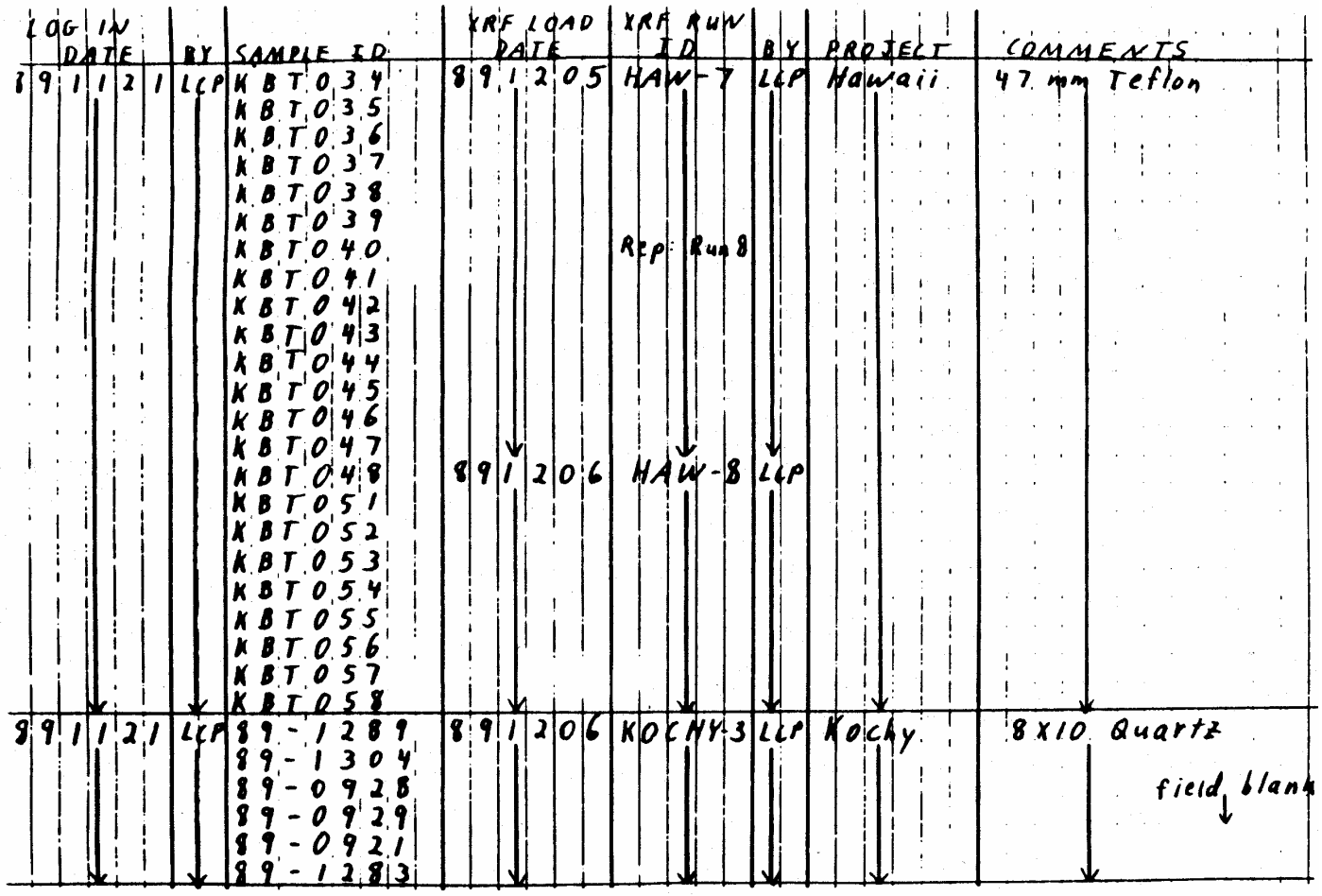


Figure 2-8. Format of XRF Analysis Logbook.

DRI X-RAY FLUORESCENCE ANALYSIS OF AIR FILTERS
LOG SHEET

		Initial	Date	Disk	Library
Project Santa Barbara	Load	LCP	891019		
Run ID SABA-26	Analyze	LCP	891019	093	SABA8.KVX
Protocol A	Unload	LCP	891019		
Blank ID BLANK-SABA3	Backup	LCP	891021	092	SABA8.KVX
Filter Dia 47 mm	SPECTRA	LCP	891020		
Filter Type Teflon	TRANSFER	LCP	891020		
Deposit Area 13.8 cm2	PRXRF	LCP	891020		
	QA Chks	CAF	891108		

QA	SO45	Sn(1)	Fe(2)	Fe(3)	Ca(3)	Ca(4)	Si(5)	
	Max	15319	46937	108377	32530	41479	23249	Gross Counts
	Meas	14998	45962	105586	31716	40255	22371	Chk OK-LCP
	Min	14427	44203	102064	30635	39062	21895	

Replicate	Orig Fe(3)	Rep Fe(3)	Diff [<3* √cts or <10%]	
GT2062	13670	14167	497 ~4%	Chk OK-LCP
				Chk

Position	Sample ID	Flg	
0	SABA-26		
1	MT4059	i4	Black specs
2	MT4060		
3	MT4061		
4	MT4062		
5	WT3039		
6	WT3040		
7	WT3041		
8	WT3042		
9	WT3043		
10	GT2062-R	rl	
11			
12			
13			
14			
15			

Rev. 8/89/bb

Figure 2-9. Example of XRF Analysis Logsheet.

As analytical runs are started, entries are made in the XRF Analyzer Logbook, as shown in Figure 2-10. The run date, data library destination, data disk number, and technician's initials are recorded both in the XRF Analyzer Logbook and on the analysis logsheet.

Maintenance performed on the XRF analyzer, including weekly filling of the analyzer with liquid nitrogen (LN2) and cleaning of disk drives, will be recorded in the XRF Maintenance Logbook as shown in Figure 2-11.

All new disks formatted and initialized are recorded in the XRF Disk Logbook (Figure 2-12). In addition, when disks are removed from the XRF room for archival purposes, this is also noted in the XRF Disk Logbook.

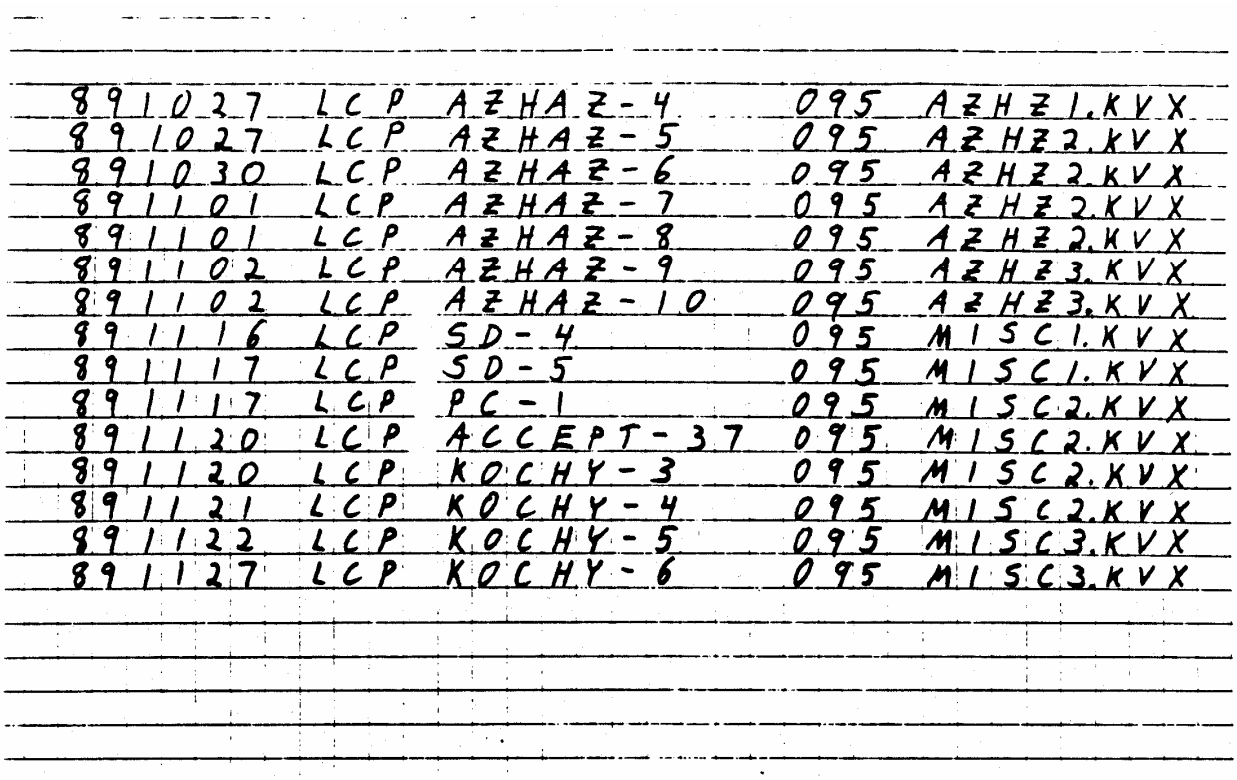
3.0 CALIBRATION STANDARDS

3.1 Preparation, Ranges, and Traceability of Standards

Three types of standards are used with the DRI XRF: elemental thin film standards from μMatter, multiple element thin film standards from μMatter, and NIST certified thin film standards. None of these standards require preparation; they are used as received from the supplier. The μMatter standards are stored in PetriSlides and kept in a freezer when not in use to retard oxidation and loss of volatile elements. NIST standards are stored in the XRF room in the sample cabinet at ambient conditions.

The μMatter thin film standards currently used at DRI are summarized in Table 3-1, including DRI Standard IDs, elements present on each standard, and the concentrations in $\mu g/cm^2$ for each element. Note that several of the standards include the same elements in different concentrations and in different combinations. Certificates of elemental concentrations are provided by the manufacturer and are filed in the XRF supervisor's office.

Two NIST thin film standards are available: SRM 1833 has certified concentrations for silicon (Si), potassium (K), Ti, Fe, zinc (Zn), and lead (Pb). SRM 1832 has certified concentrations for Al, Si, calcium (Ca), vanadium (V), manganese (Mn), cobalt (Co), and copper (Cu).



891027	LCP	AZHAZ-4	095	AZHZ1.KVX
891027	LCP	AZHAZ-5	095	AZHZ2.KVX
891030	LCP	AZHAZ-6	095	AZHZ2.KVX
891101	LCP	AZHAZ-7	095	AZHZ2.KVX
891101	LCP	AZHAZ-8	095	AZHZ2.KVX
891102	LCP	AZHAZ-9	095	AZHZ3.KVX
891102	LCP	AZHAZ-10	095	AZHZ3.KVX
891116	LCP	SD-4	095	MISC1.KVX
891117	LCP	SD-5	095	MISC1.KVX
891117	LCP	PC-1	095	MISC2.KVX
891120	LCP	ACCEPT-37	095	MISC2.KVX
891120	LCP	KOCHY-3	095	MISC2.KVX
891121	LCP	KOCHY-4	095	MISC2.KVX
891122	LCP	KOCHY-5	095	MISC3.KVX
891127	LCP	KOCHY-6	095	MISC3.KVX

Figure 2-10. Format of XRF Analyzer Logbook.

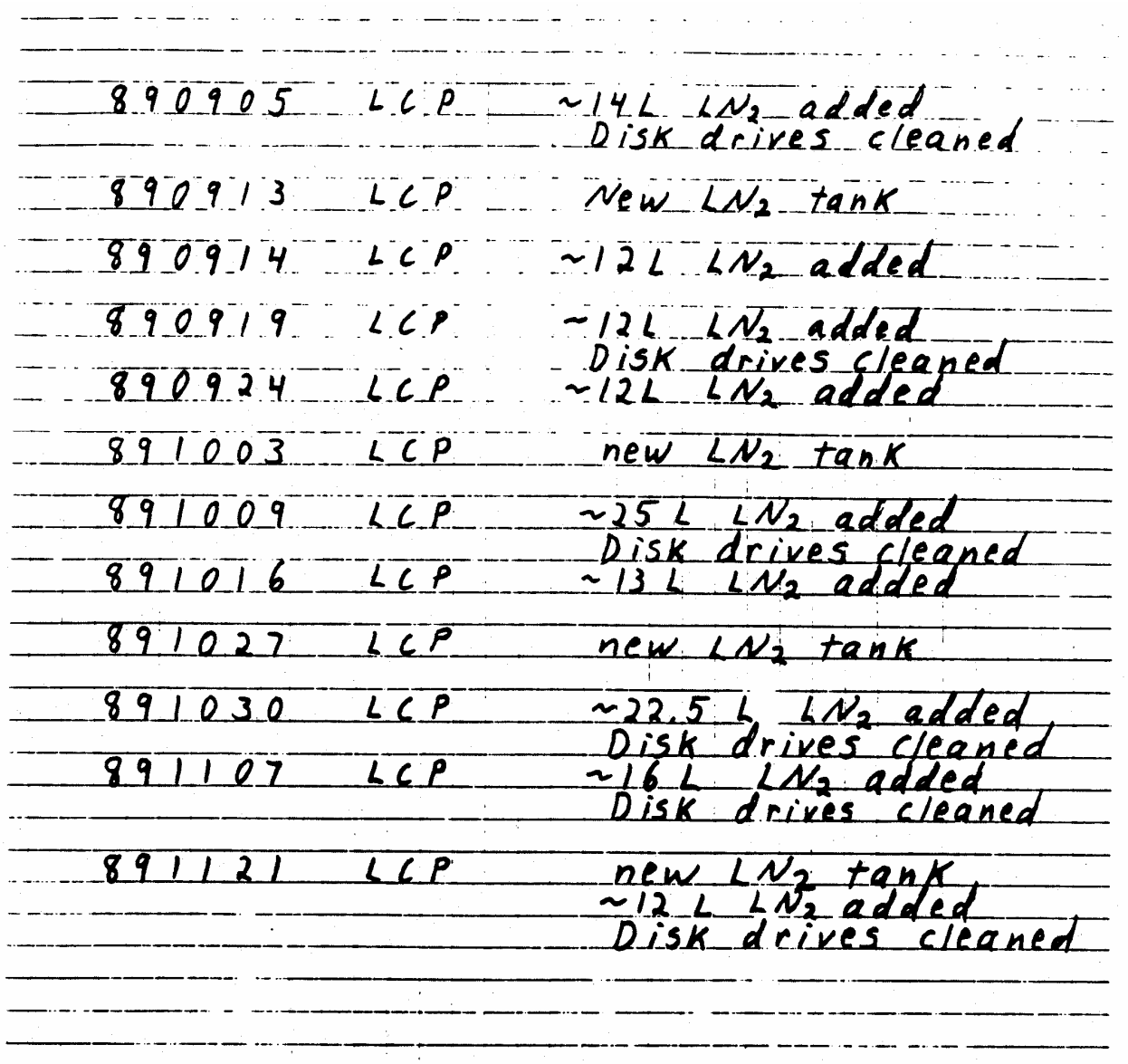
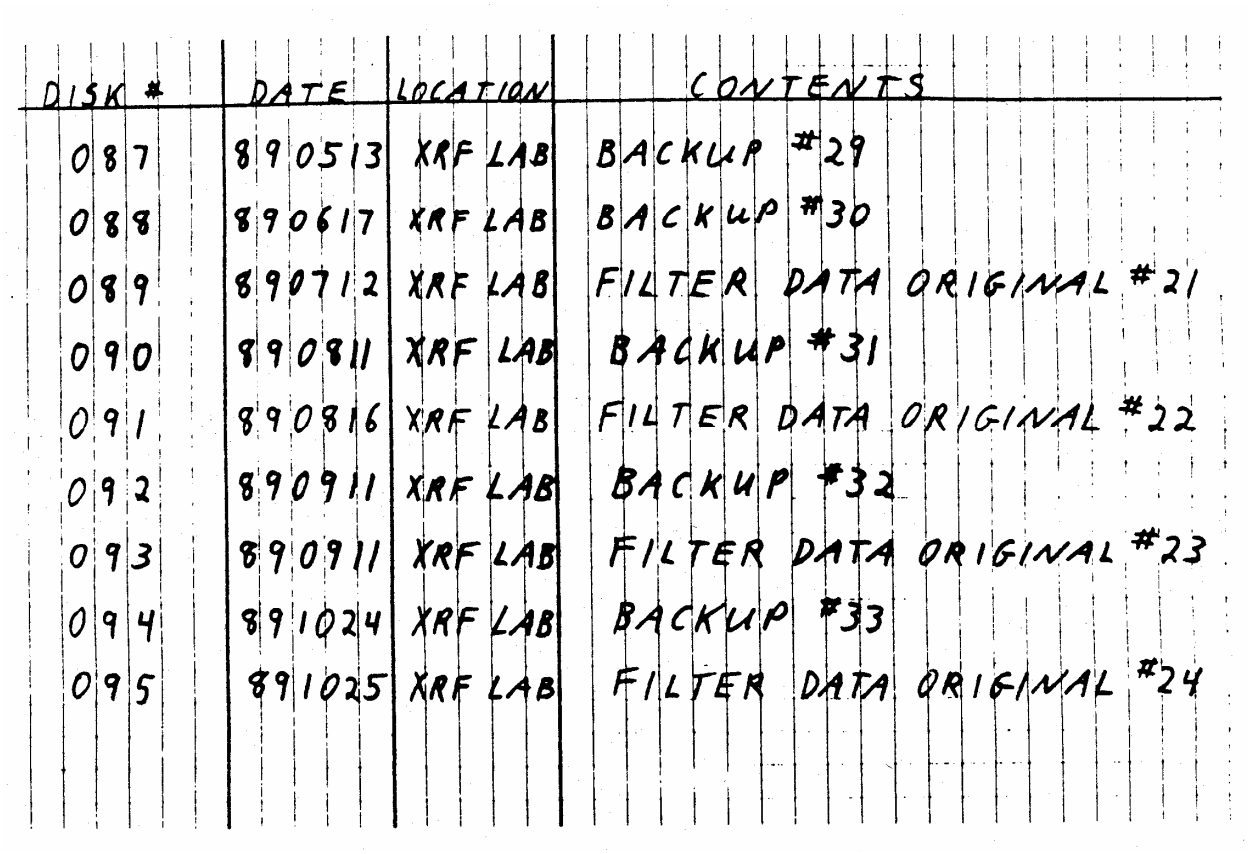


Figure 2-11. Format of XRF Maintenance Logbook.



DISK #	DATE	LOCATION	CONTENTS
087	890513	XRF LAB	BACKUP #29
088	890617	XRF LAB	BACKUP #30
089	890712	XRF LAB	FILTER DATA ORIGINAL #21
090	890811	XRF LAB	BACKUP #31
091	890816	XRF LAB	FILTER DATA ORIGINAL #22
092	890911	XRF LAB	BACKUP #32
093	890911	XRF LAB	FILTER DATA ORIGINAL #23
094	891024	XRF LAB	BACKUP #33
095	891025	XRF LAB	FILTER DATA ORIGINAL #24

Figure 2-12. Format of XRF Disk Logbook.

Table 3-1
μMatter Thin Film Standards Used at DRI

DRI ID	Element	Concentration (μg/cm^2)
S062	Na	19.0
S024	Mg	34.6
S067	Mg	38.4
S047	Al	43.2
S026	Si	28.1
S001	P	13.6
S001	Ga	26.0
S002	S	15.5
S002	Cu	47.5
S051	S	15.7
S058	S	15.0
S003	Cl	16.8
S004	Cl	25.4
S004	K	25.5
S065	K	25.4
S005	Ca	25.2
S006	Ti	42.4
S007	V	30
S008	Cr	39.9
S009	Mn	54
S010	Fe	73
S011	Co	70
S012	Ni	34
S035	Zn	8.19
S038	As	4.68
S016	Se	48
S017	Br	19.9
S039	Rb	7.76
S040	Sr	4.72
S053	Y	28.6
S037	Zr	10.6
S042	Mo	36.7
S054	Pd	30
S021	Ag	20
S021	Hg	45
S019	Cd	41
S070	Cd	27.2
S055	In	47
S020	Sb	23
S038	Ba	4.76
S056	La	37.6
S061	Au	43
S060	Hg	32.6
S022	Tl	40.9
S023	Pb	66
S073	Pb	47.1
S074	U	23.0

3.2 Use of Standards

Prior to their use for calibration, the accuracy of all standards is verified. This is accomplished by analyzing the standards and plotting instrument response, in counts per second per $\mu g/cm^2$ versus atomic number. This results in a smooth curve. If response for a given standard is not on the curve (>5% deviation), its stated concentration is incorrect, and the standard is returned to the manufacturer for replacement.

The DRI XRF system is recalibrated every three months using the μMatter thin film standards. Recalibration is also performed whenever the QA standard indicated a drift of >±3% in calibration. Standards including elements from Na to U are analyzed in standard 37 mm filter holders under the standard analysis program (FILTER; see Section 4). Calibration factors in $\mu g/m^2$ per counts per second are extracted for inclusion into the PRXRF program (Sections 5.1 and 5.2). Calibration accuracy is checked by analyzing the NIST standards.

3.3 Typical Accuracy of Calibration Standards

The μMatter standards are accurate to ±5% relative, as stated by the manufacturer.

4.0 PROCEDURES

4.1 General Flow Diagram

The typical flow of samples and data for DRI XRF analysis is depicted in Figure 4-1.

4.2 Analyzer Start-Up

Normally the Kevex XRF 0700 and 8000 units are left running at all times and require no special starting procedure. However, if the power has been interrupted, the computer and Multi-Channel Analyzer (MCA) require initialization before analysis may begin. The following steps outline analyzer start-up:

4.2.1 Computer Initialization

- Power is applied to the 0700 computer via a switch on the top of the Bernoulli disk drives. Insure that no disks are in either drive, and turn the switch on.

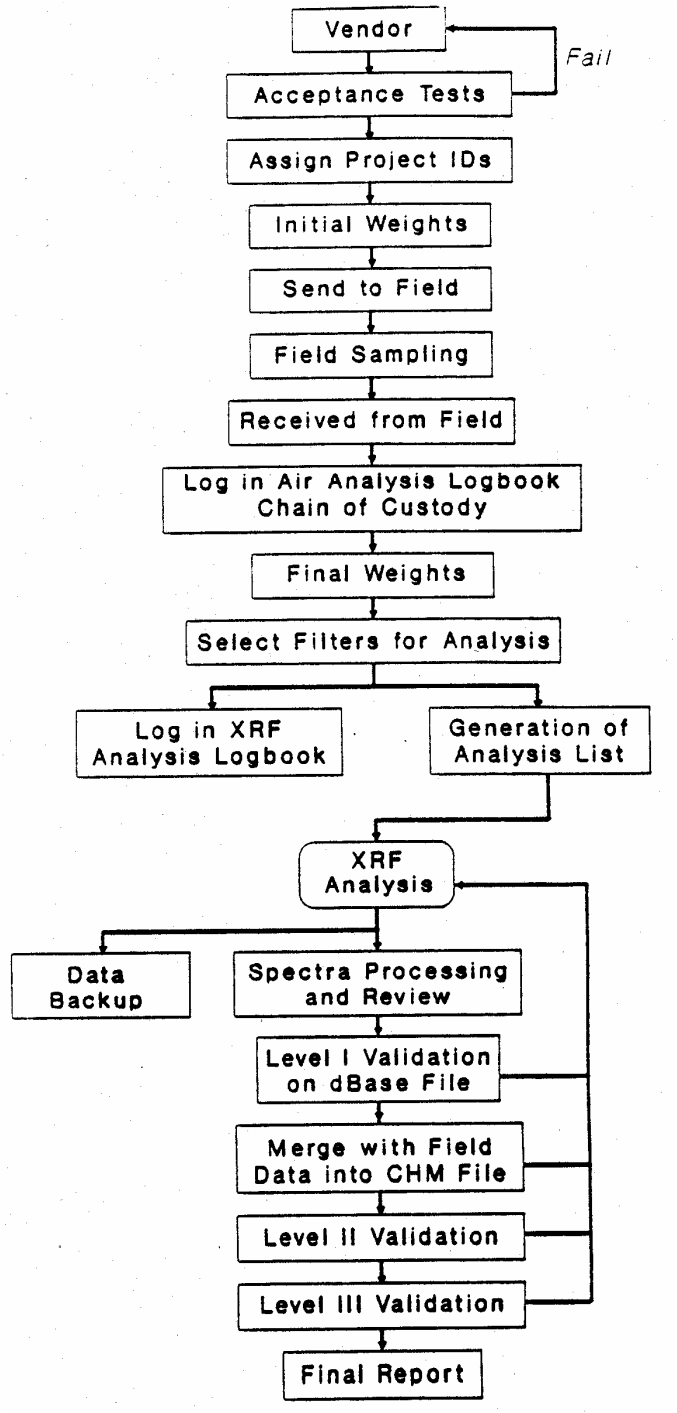


Figure 4-1. Flow Diagram of XRF Sample Processing.

- The computer will perform an internal self-test, resulting in a message "KEVEX Cold Start" on the screen. If the screen remains dark, try adjusting the screen intensity with the left knob on the monitor pedestal.

- Place the current program disk in the bottom drive (drive 0) by orienting the disk with the label indent to the right and slowly pushing the disk in. Close the drive door by pushing it to the right until it latches. The green light on the drive should illuminate within 10 seconds.

- Press the **<Program>** firmware key on the 8000 keyboard. A menu will appear with several options. Press **<5>** (System Setup) followed by a **<Return>**. A second menu will appear; again press **<5>** (Boot DEC computer) followed by a **<Return>**. The menus will disappear and the message "<BOOT>" will appear on the screen. Press the **<Return>** to initiate the booting procedure. The disk drive access light will come on and the software copyright notice will be displayed after about 30 seconds. If the disk does not boot correctly, cycle power to the computer and try again. To cycle power to the computer, remove the disk from the drive, remove the front panel cover under the keyboard, turn the switch labeled **CPU** off, wait 15 seconds, then turn the switch back on.

- After a copyright notice appears on the screen, the file loading utility menu appears (Figure 4-2). Press **<Return>** to load Toolbox (the default option is "X", which loads Toolbox).

- A screen presenting three MCA options will appear on the screen (Figure 4-3). The cursor will be pointing to the middle option by default. Press **<Return>** to select this option. A number of progress messages will appear on the screen as Toolbox and supporting data is loaded. When the "*" prompt appears, the system is ready to run programs.

- After the main terminal (the 8000 terminal) has completely loaded Toolbox and presents an "*" prompt, the remote terminal must be initialized as well. Turn the IBM XT on. After the "C>" prompt appears, type **CD XTALK** to change to the CrossTalk subdirectory.

- On the remote terminal, type **XTALK KEVEX** to start the CrossTalk communications program and to begin VT-100 terminal emulation. When a screen is presented with only a status bar on the bottom, the remote terminal is active through the XT keyboard.

- Press **<Return>** at the XT keyboard. The Kevex copyright notice will appear, followed by the file loading utility menu (Figure 4-2). Press **<Return>** to load Toolbox.

- A screen presenting the three MCA options will appear on the screen (Figure 4-3). Use the down-arrow key to place the cursor at the third (bottom) option (virtual MCA). NOTE: do not select the middle option from the remote terminal; if such a selection is made, both the 8000 terminal and the remote terminal think they have control over the hardware MCA, and the system will crash. If such a selection is made, the 8000 computer MUST be completely powered down and the cold start procedures presented in this section followed again.

- Press the **<Return>** on the remote terminal to select the third MCA option. When the "*" prompt appears on the screen, the remote terminal is ready for use. NOTE: at several times during the initialization of the remote terminal, the cursor on the 8000 terminal may disappear. The cursor on the 8000 terminal may be restored after the remote terminal has finished initializing by pressing **<Return>**.

4.2.2 X-ray Tube Startup

- Power to the 8000 x-ray cabinet is controlled by use of a key switch on the front of the cabinet (Figure 2-1). Insure that the vacuum pump control is "off" and the air flow switch is at the "vent" position, and turn the key to the "on" position.

- Switch the pump control switch to the "on" position to allow the vacuum pump to begin removing oil vapors from connecting lines and to reach an operating temperature.

- Switch the Mode Switch to the "manual" position. Tap the kV button to allow entry of "10" at the numeric keypad. If a mistake in entry is made, simply continue typing the correct entry; the erroneous digits will scroll off the display to the left. When the entry is correct, press the **<Enter>** key. The red safety beacon should light and the x-rays lights will begin blinking.

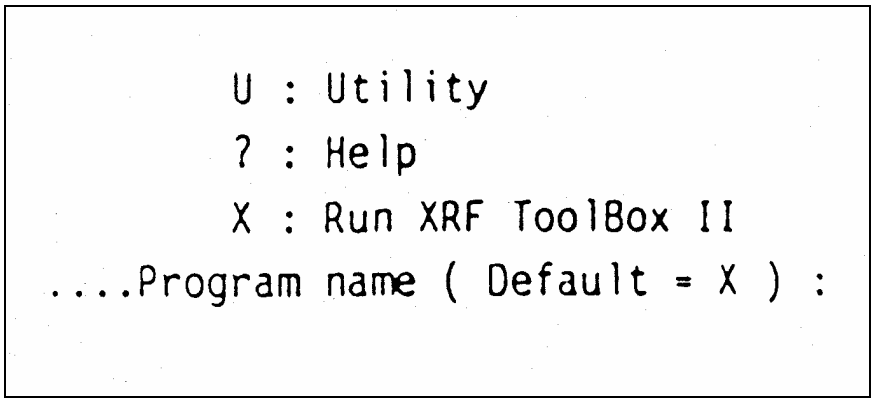


Figure 4-2. File Loading Utility Menu.

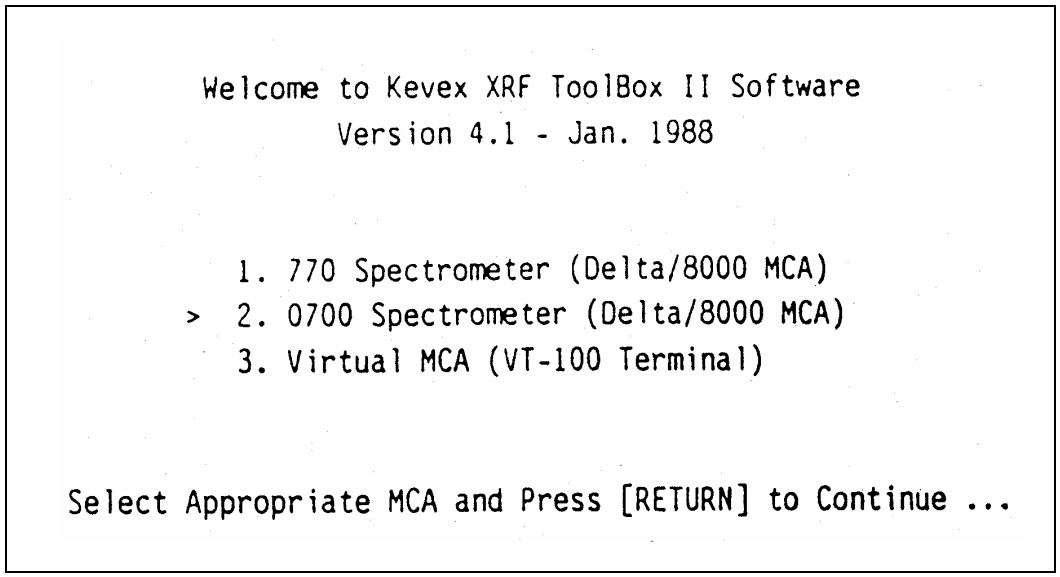


Figure 4-3. XRF MCA Options Menu.

- Tap the mA button to allow entry of "0.20" in a similar manner. Note that subsequent taps of the mA button will shift the decimal point to one of two positions. Press the **<Enter>** key when the entry is correct.

- The display selector switch should be set to the "kV" position. Within 20 seconds the display should reach "10.0" or "10.1". If not, press the red **<Reset>** button momentarily. Insure that the cabinet cover is completely settled in the down position and repeat the previous two steps. If the x-ray tube still does not indicate a voltage, notify the XRF supervisor. NOTE: the red safety beacon must be in working condition for the x-ray tube to be energized. If problems are experienced with the x-ray tube failing to energize, check this bulb first. It should be replaced with a 60 W 110 VAC if defective.

- The x-ray tube must be allowed to warm at this setting (10 kV and 0.20 mA) for at least one hour. Attempts to ramp the voltage and current to higher values when the tube is cold will result in internal arcing, and the 8000 unit will shut off the tube. This arcing is not good for the tube, and all efforts should be made to avoid premature increase in tube voltage until the tube is thoroughly warm. After one hour, increase the voltage and current in steps:

10 kV	0.20 mA	≥ 60 minutes
20 kV	0.40 mA	10 minutes
30 kV	0.60 mA	10 minutes
40 kV	0.80 mA	10 minutes

  (If starting up the system after a short power outage of 5 minutes or less, the tube needs to stay at 10 kV and 0.20 mA for only 10 minutes, and subsequent steps can be made at 5 minute intervals.)

- The MCA and associated electronics must be allowed to completely warm and stabilize for one hour before the energy calibration is attempted. This warmup will take place as the tube is warming up.

4.2.3 Energy Calibration

The MCA must be calibrated for the signals coming from the detector in order that they be placed in the properly labelled energy channels. This recalibration step is only necessary when electrical power to the MCA has been removed, as the MCA normally stores the energy calibration factors. The energy calibration is gauged using a 316 stainless steel disk and using iron K α line at 6.400 and the Mo K α line at 17.443.

- Using a large Kimwipe and methanol, wipe the working surface of the sample preparation table to remove loose dust. Place a large Kimwipe on the table in this cleaned area.

- Locate the small wooden box containing the Kevex standards in the XRF sample cabinet. Remove the SS316 metal disk from the box and place it into the specially machined plexiglass holder also found in the box. Place it such that the metal surface is down and the red

label is on top. Place the holder/metal disk combination on the clean Kimwipe.

- Manually ramp down the x-ray tube voltage and current to 10 kV and 0.20 mA, going in steps of 10 kV and 0.20 mA. In other words, go through the following steps:

40 kV	0.80 mA	(warm-up and tube idle conditions)
30 kV	0.60 mA	
20 kV	0.40 mA	
10 kV	0.20 mA	(minimum conditions)

  As each entry is input, the displays besides the kV and mA buttons will flash until the tube has reached the new conditions. During the time that these displays are flashing, the kV and mA buttons are locked and will not accept new entries. NOTE: THE TUBE MUST BE RAMPED UP AND DOWN IN SMALL STEPS TO PREVENT ELECTRICAL STRAIN ON THE X-RAY TUBE AND THE POSSIBILITY OF INTERNAL ARCING.

- When the x-ray tube has reached 10 kV and 0.20 mA, press the red reset button to turn off the x-rays. When the tube voltage has reached 0.0 kV, double check that x-rays are indeed off: the red beacon light should be off, the four "X-Ray/On" lights on the front panel should not be blinking, and the voltage reading should be 0.0. If any of these conditions is not met, contact the XRF Supervisor before proceeding. Insure that the Air Flow switch is in the "vent" position and open the cabinet cover until it latches. Take care not to drop the cover. The pressure change and physical shock may rupture the Be window.

- Place the holder/metal disk combination into sample position 1 in the sample carousel, taking care to avoid "dropping" the holder into position and to avoid disturbing the carousel more than necessary. UNDER NO CIRCUMSTANCES hold the holder/metal disk combination over the QA sample in position 0; the beryllium detector window is immediately below the QA sample, and dropping the metal disk would rupture the window. See Section 2.1.2.

- Carefully close the cabinet cover by supporting the cover with one hand and pulling the bottom of the latch at the back of the cabinet with the other hand; allow the cover to close gently. Turn on the x-ray tube by entering a tube voltage of 10 kV and a tube current of 0.20 mA. Note: when the kV and mA buttons are pushed, the most recent manual kV and mA entries will appear in the numeric display. Simply push **<Enter>** to accept those values.

- Do not turn the Air Flow switch to the "vacuum" setting (the chamber remains at ambient pressure).

- Ramp the x-ray tube to 40 kV and 1.1 mA in even intervals of 10 kV and 0.3 mA.

- Select tray position 1 by pressing the Sample Position button and entering 1 on the numeric keypad. Press **<Enter>** to move the metal disk over the detector.

- Move the Mode Switch to the "Auto" position.

- Move to the 8000 keyboard and press the **<Setup>** firmware key. From the menu that appears (Figure 4-4) select option 2 (Acquire) by pressing **<2> <Return>**. From the subsequent menu (Figure 4-5) select MCA memory 1 by pressing **<1> <Return>**. Select the appropriate item numbers (Figure 4-6) to change the entries to:

  4.5 second time constant
  100 sec acquisition time
  20 kV range

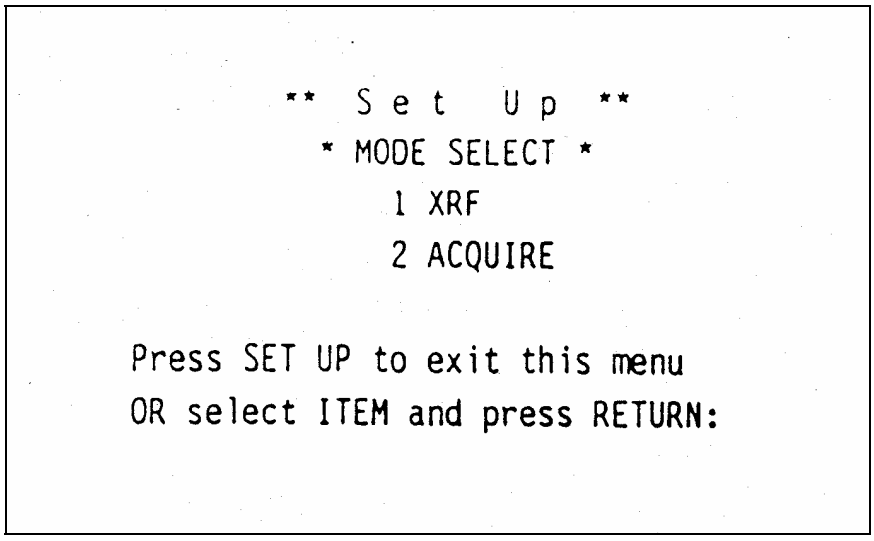


Figure 4-4. XRF Setup Option: Level 1 Menu

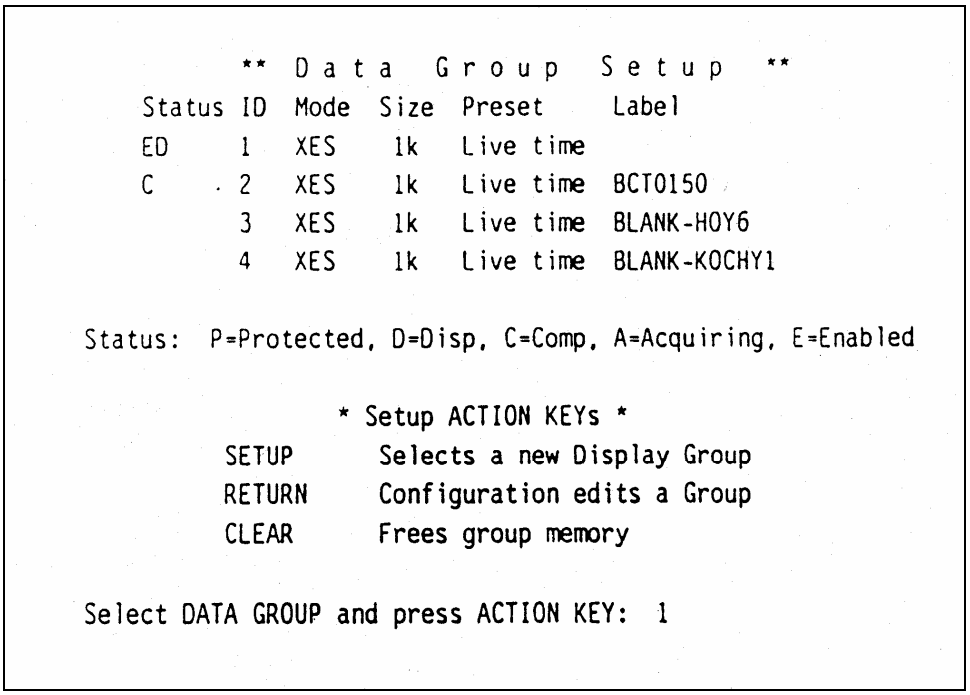


Figure 4-5. XRF Setup Option: Level 2 Menu.

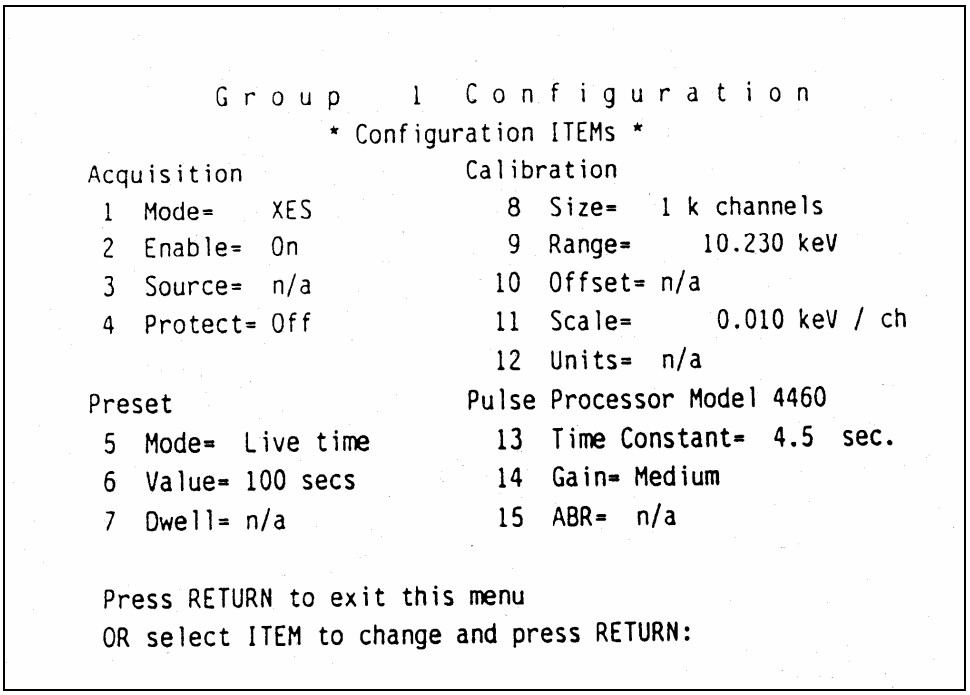


Figure 4-6. XRF Setup Option: Data Collection Parameters.

Press the **<Setup>** firmware key again to return to the main screen.

- Press the **<Filter/Target>** firmware key. Press the space bar to toggle to the second half of the screen and select Ag secondary target by typing **<3> <Return>**. The target/filter display on the 0700 x-ray cabinet should read 03. Press **<Filter/Target>** again to return to the main screen.

- Press the **<Program>** firmware key. Select option 4 (self-test) from the menu that appears (Figure 4-7) by pressing **<4> <Return>**. Select option 4 (EDC calibration) from the second menu (Figure 4-8) by pressing **<4> <Return>**. From the third menu (Figure 4-9) select the appropriate item numbers to change the entries on the screen to:

  0.003 accuracy
  5 keV minimum peak separation
  6.400 low peak value
  17.443 high peak value

- From the same menu, select option 7 to clear the MCA by pressing **<7> <Return>**.

- From the same menu, select option 1 to begin auto-calibration by pressing **<1> <Return>**.

- The program will automatically collect data for 100 seconds live time, check the positions of the two peaks, readjust the gain and zero of the MCA, and begin another iteration. As soon as the peaks' positions are properly adjusted, the message "Calibration Complete" will appear on the screen. Note: the system typically requires 3 to 10 iterations of collecting data to properly calibrate itself. When the calibration is complete, press the **<Program>** firmware key to return to the main screen.

- Press the **<Filter/Target>** firmware key and select options 0 for the right half of the screen by pressing **<space bar> <0> <Return>**. Press the **<Filter/Target>** key again to return to the main screen.

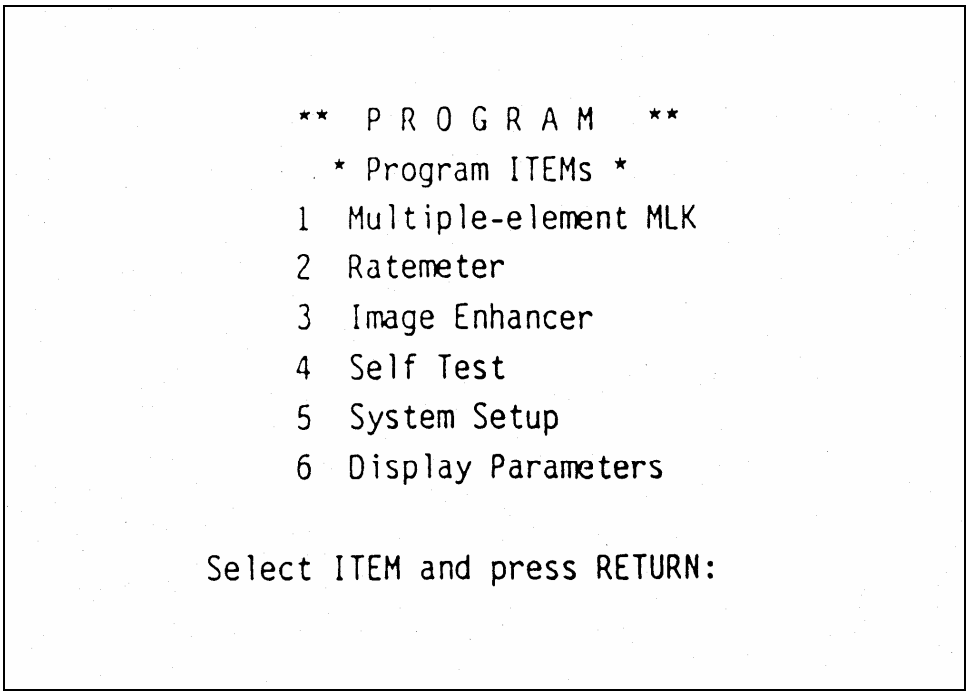


Figure 4-7. XRF Program Option: Level 1 Menu.

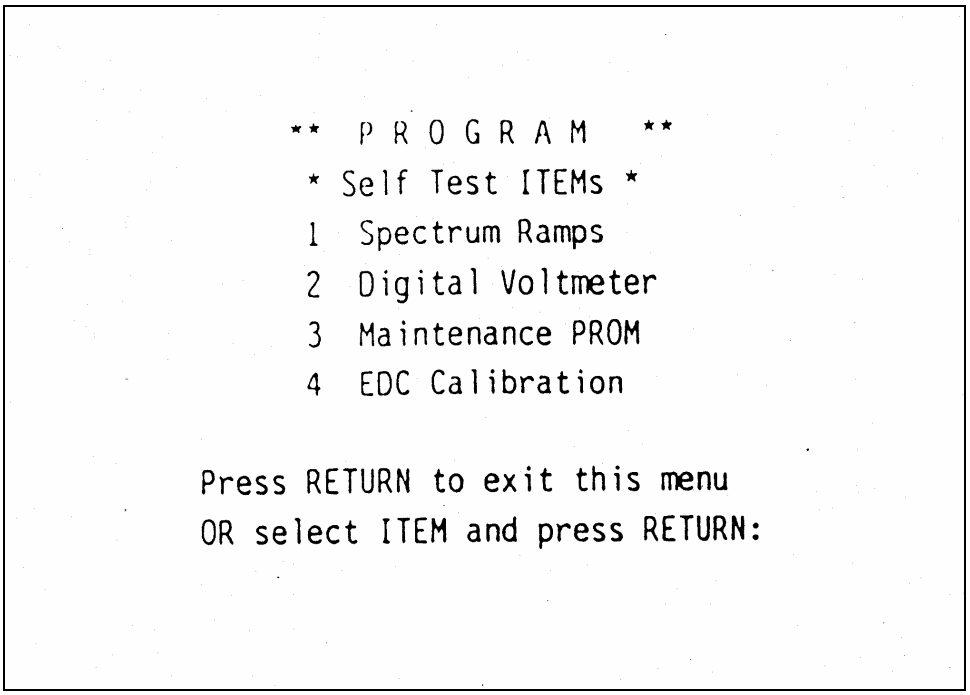


Figure 4-8. XRF Program Option: Level 2 Menu.

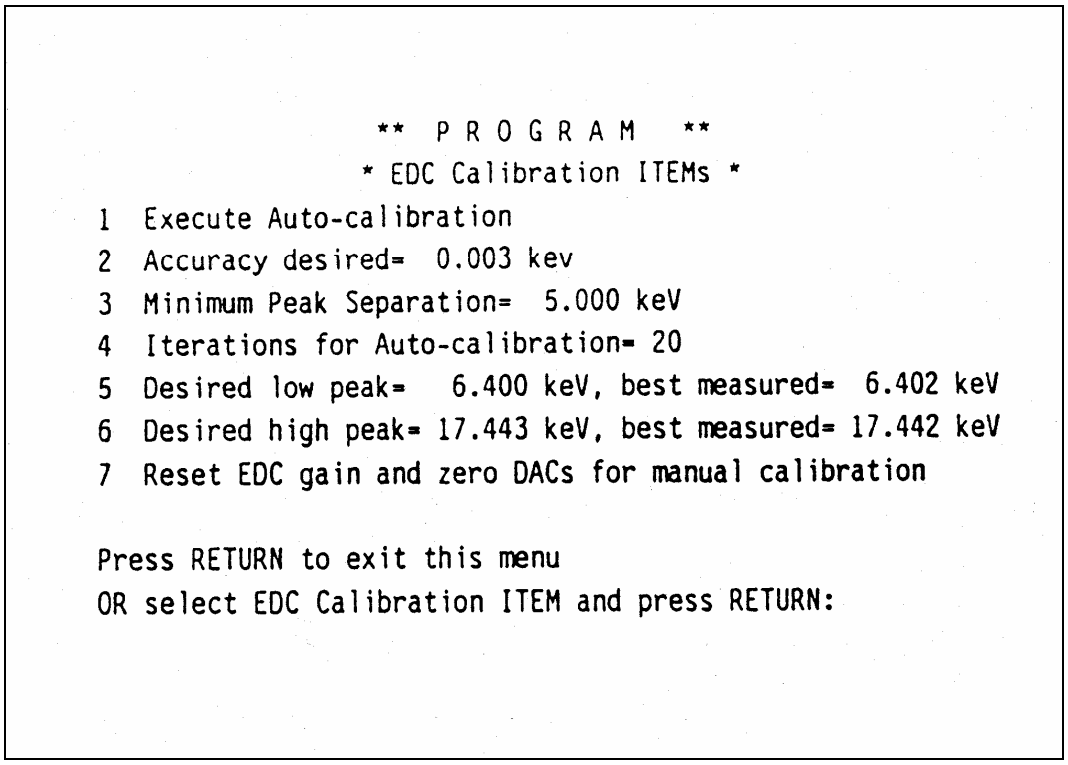


Figure 4-9. XRF Program Option: Calibration Parameters.

- Move the Mode Switch to the "manual" position. Return the sample carousel to position 0 by pressing the Sample button and entering "0" on the numeric keypad followed by the **<Enter>** key.

- Ramp the tube voltage and current to 10 kV and 0.20 mA, respectively.

- Press the red reset button to turn off the x-ray tube. When the indicated kV reading has dropped to 0.0, double check that x-rays are off as described above, and open the cabinet cover. Carefully remove the holder/metal disk assembly and place it on the Kimwipe. Close the cabinet cover and energize the x-ray tube by setting it to 10 kV and 0.20 mA.

- Return both the metal disk and the sample holder to the wooden box and return the box to the XRF sample cabinet.

- Samples may now be loaded using the procedure described in Section 4.3. If samples will not be analyzed immediately, return the x-ray tube to its idle conditions by ramping the tube voltage and tube current to 40 kV and 0.80 mA, respectively.

4.3 Routine Operation

The steps for routine analysis are summarized in Figure 4-10. The following sections describe in detail these steps. This section must be read and understood in its entirety before beginning sample analysis. When all aspects of the analysis procedure are understood, the abbreviated checklist appearing in Section 4.5 may be used for reference.

4.3.1 Filter Log-in

Samples designated for XRF analysis are identified in a sample analysis list produced by the Laboratory Supervisor (Figure 2-7). These lists identify the samples to be analyzed, which samples are lab and field blanks, the deposit areas to be used, the XRF analysis run ID, the date that analysis should begin, and the name of the final dBase file. Samples are typically taken to the XRF room at the same time the analysis list is delivered. Samples are placed in the XRF sample cabinet; they are labelled by a note taped to the front of the shelf which identifies the project and

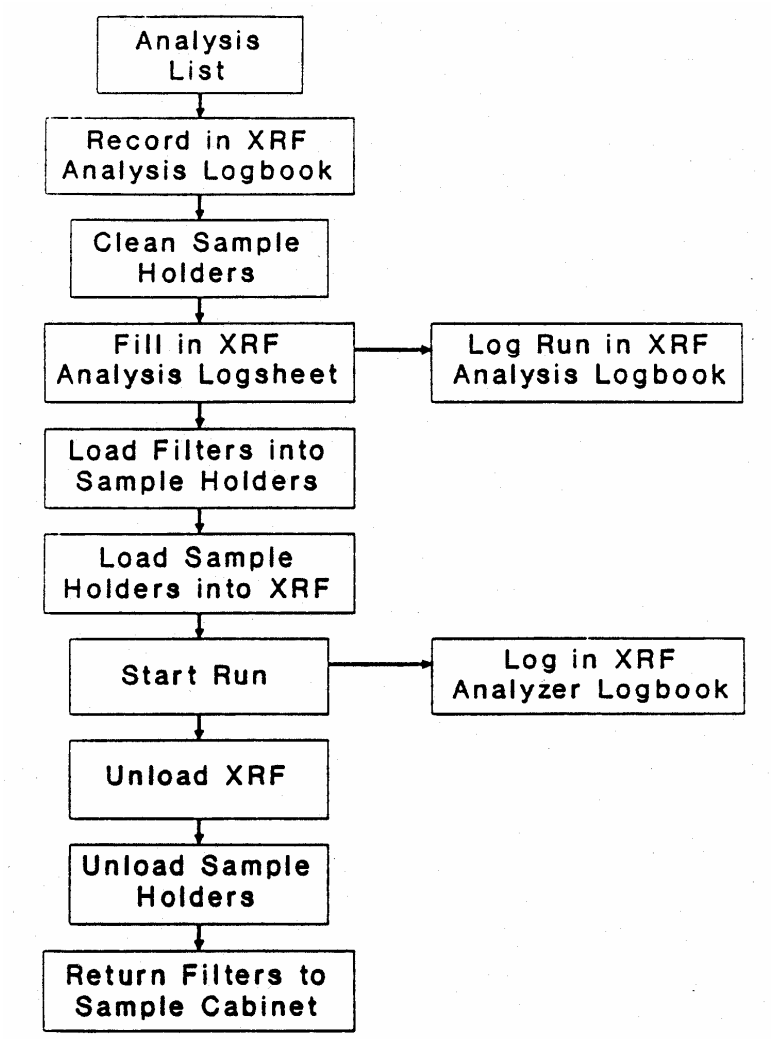


Figure 4-10. Flow Diagram for XRF Analysis.

the phrase "To Be Analyzed". The analysis list is left on the work table to indicate that these are new arrivals and need to be put in the queue for analysis.

Samples are recorded from the analysis list into the current XRF Analysis Logbook using the format in Figure 2-8. All samples must be recorded in this logbook upon arrival in the XRF room so that the current analysis status can be determined by referring to the logbook.

The sample analysis list is taped to the XRF sample cabinet after the samples have been recorded in the XRF Analysis Logbook.

4.3.2 Filter Loading

The filter loading procedure depends on the filter media to be analyzed. The procedures are different for these two options. The XRF Supervisor may designate special handling and loading procedure for unusual samples or project requirements. The notes at the top of the analysis list should be read carefully before handling the samples.

Glass-fiber or quartz filters are infrequently analyzed at DRI by XRF for elements heavier than sulfur. Sulfur and lighter elements cannot be measured quantitatively on glass fiber or quartz filters due to high, variable background levels of these elements on these filter media and due to high absorption and backgrounds resulting from the relatively thick filter media.

Glass fiber and quartz filters are most frequently in the form of 8" X 10" sheets used in hi-vol samplers. Sample punches are taken from these large sheets for analysis in the following manner:

- A large Teflon cutting surface and a 9.5 cm^2 sample punch are obtained from the XRF sample cabinet and cleaned thoroughly with methanol-dampened Kimwipes. Caution: the cutting edge of the punch is sharp enough to easily cut Kimwipes and fingers.

- Put on a pair of latex gloves and wipe with a methanol-dampened Kimwipe to remove loose particles.

- Label a PetriSlide with the ID number of the first filter.

- Remove the first filter from its envelope or folder. Handling it by the edges, open it and lay it on the Teflon cutting surface.

- Select an area at one corner which is typical of the deposit as a whole and which is approximately 1-2 cm from the deposit edges. Avoid areas of uneven deposit. Do not select an area too close to the edge to avoid deposit inhomogeneities. Try to stay at the edge of the deposit within these constraints to avoid damaging any more of the deposit area than necessary.

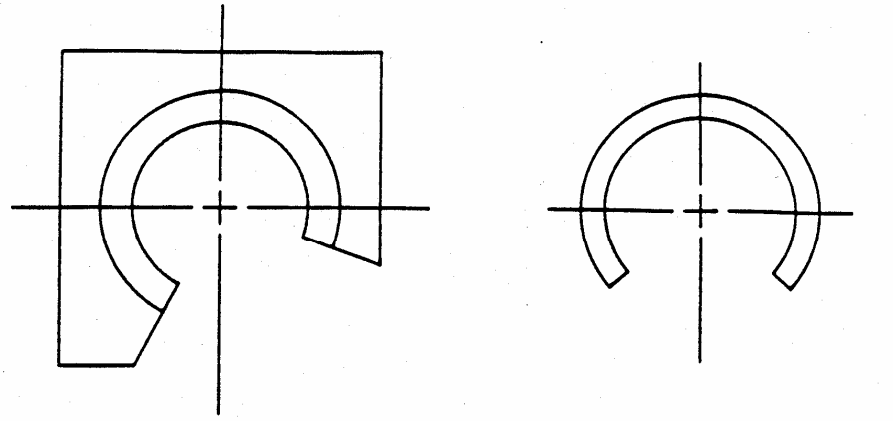
- Firmly place the punch onto the selected area. The punch may be rocked slightly to insure that all edges have been severed. The filter punch is

removed from the punch with tweezers (handle only at the extreme edges) and placed into a pre-labelled PetriSlide.

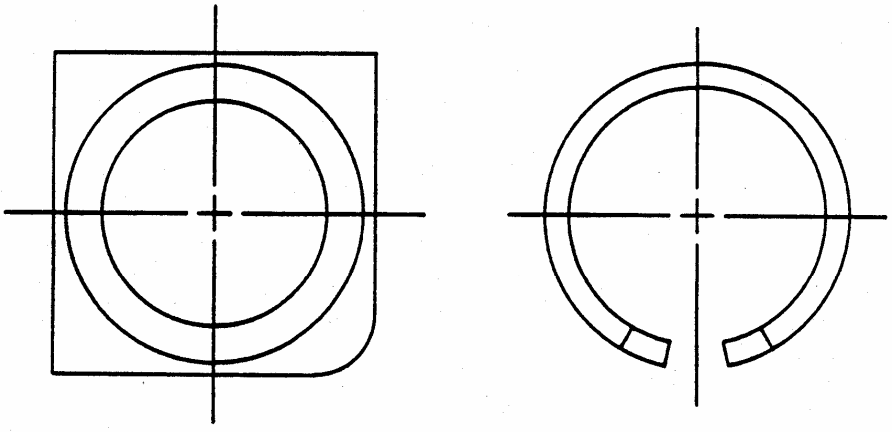
- Double check that the ID number on the filter envelope or holder matches the PetriSlide ID number.
- Refold the filter and return to its original folder or envelope.
- Clean the cutting surface, punch, tweezers, and gloved fingertips thoroughly between samples.
- Continue in a similar manner for the remaining samples.

Teflon membrane filters analyzed at DRI are generally 37, 42, or 47 mm diameter ring-mounted filters. The sample holders used in the DRI XRF are custom-designed holders for 37 or 47 mm filters (Figure 4-11); the 42 mm filters will fit in the 47 mm holders if loaded carefully. Sample punches of glass fiber or quartz filters using DRI's sample punch are placed into 47 mm holders. Other sizes of filters may be accommodated; refer to the analysis list or XRF Supervisor for additional instructions.

Both the 37 and 47 mm holders are designed to fit in the 2" by 2" holder positions in the XRF sample carousel. Both styles consist of two parts: a holder base and a friction-fit retainer ring. The 37 mm holders are designed with a large "missing" corner; this large gap prevents the incident x-rays, which approach the filter at an angle, from reflecting off the filter holder plastic at that corner and adding to the background scatter on the spectra. This



37mm XRF FILTER HOLDER



47mm XRF FILTER HOLDER

Figure 4-11. Diagram of DRI 37 and 47 mm XRF Sample Holders.

feature is necessary due to the small opening in the filter holder base with respect to the x-ray beam spot. The 47 mm holder bases have one rounded corner which is necessary to fit the shape of the openings in the sample carousel. The 47 mm holders are not missing one corner, as their openings are already large enough to minimize backscattering effects.

The holders are labelled in the lower right corner with a number between 1 and 15 which corresponds to a position in the sample carousel; the retainer rings are not numbered. Select a complete set of holder bases and retainer rings for positions 1 through 15.

Filters are loaded in the following manner:

- Wipe the work area clean with a methanol-dampened Kimwipe. Stretch a large Kimwipe towel across the work area and secure it to the table top with tape. Insure that creases and wrinkles are removed. Because the filters are loaded into the holders face down, all wrinkles and protrusions must be removed to avoid damaging the filter deposits.

- Using latex gloves which have been carefully wiped with a methanol-dampened Kimwipe after being slipped on (to remove loose particles from the gloves), carefully wipe each sample holder base and retainer ring with methanol-dampened Kimwipes. Insure that all surfaces are free of particles, particularly the inner lip of the holder bases and the side of the retainer ring which will be contacting the filter. Take care not to wipe the number from the corner of the holder bases. Place the holder bases on the clean Kimwipe in three rows of 5 holders each; place the cleaned retainer rings on top of the holder bases. Holders numbered 1 - 5 are in the top row, left to right, 6 - 10 in the second row, left to right, and 11 -15 in the bottom row, left to right.

- After all holders and retainer rings have been wiped clean, remove the gloves and wash hands to remove any traces of talc or excess perspiration.

- Referring to the XRF Analysis Logbook, select 15 filters for analysis. The first two analysis runs for a particular project will include 15 first-time analyses and no replicates. Subsequent runs will include replicates at the rate of 2 per run for one run, followed by 1 replicate per run for two runs. By following this pattern approximately 10% replicates will be run. Final adjustments in the number of replicates run are made in the final run for a given project.

- Retrieve the samples to be analyzed from the XRF sample cabinet and lay the selected filters evenly across the Kimwipe, in three rows of 5 filters each, beneath each filter holder. (The filters are still in their labeled containers at this step).

- Locate a current XRF Analysis Logsheet (Figure 2-9). Note: the QA gross counts ranges on the Analysis Logsheets change slightly every three months when the XRF is recalibrated; make sure the latest version of the Analysis Logsheet is used. Complete the project, run ID (as specified in

the analysis list), filter type and size, and sample load date and technician's initials sections as shown in Figure 2-9.

- Write the run ID in the sample ID section for position 0. This position is always occupied by the QA filter; therefore, the spectra saved under the run name will be the QA data. Complete the remaining sample IDs positions with the filter IDs selected for this run, referring to the XRF Analysis Logbook and making sure that the correspondence of holder number and sample ID is the same on the XRF Analysis Logsheet as on the loading table.

- Indicate the XRF run ID, load date, and technician's initials in the XRF Analysis Logbook for the samples selected for analysis (Figure 2-8).

- Check the filters for visual defects, large particles, filter damage, or other abnormalities which may affect the quality of the analysis. Note any problems in the comments section of the Analysis Logsheet.

- Teflon Membrane Filter Loading

  The following steps are followed to load ring-mounted membrane filters into the filter holders:

  -- After wiping a pair of tweezers clean with a methanol-dampened Kimwipe, remove the filter from the first petri dish or PetriSlide. Examine the deposit closely for defects not previously noted. Remove carefully all large or loose particles which may fall off during analysis.

  -- Carefully move the retainer ring from the corresponding holder base (avoid touching the lower surface which will contact the filter). Turn the filter over (face down) and place it into the holder base.

  -- Place the retainer ring over the filter, squeeze it slightly to reduce its circumference, and place it over the filter to hold it flat. Insure that the opening in the retainer ring is oriented toward the right. Note: the filters must be completely flat against the inner lip of the holder bases: the x-ray signal is sensitive to distance travelled, and slight changes in the distance between the x-ray tube, the filter, and the detector will have measurable effects.

  -- Proceed in a similar manner for the remaining samples.

  -- After all samples are loaded, double check that the sample ID on the Logsheet matches the ID on the empty filter container for each position.

  -- If samples will not be loaded immediately into the XRF sample chamber, place a large, clean Kimwipe over the holders and place the Analysis Logsheet on top.

  -- Proceed to Section 4.3.3.

- Quartz or Glass Fiber Filter Loading

  The following steps are followed to load glass fiber or quartz filters into the filter holders:

  -- Locate the box of Mylar sheets (3.6 μm, 2 X 2 inch squares) in the XRF sample cabinet.

  -- Open the box of Mylar and carefully remove the top tissue paper; a sheet of Mylar should accompany the tissue paper due to static attraction.

  -- Carefully move the retainer ring from the corresponding holder base (avoid touching the lower surface which will contact the filter).

  -- Place the Mylar over the first holder base. Holding one corner of the Mylar with tweezers, remove the tissue paper, leaving the Mylar draped over the filter holder.

  -- After wiping a pair of tweezers clean with a methanol-dampened Kimwipe, remove the filter from the first petri dish or PetriSlide. Examine the deposit closely for defects not previously noted. Remove carefully all large or loose particles which may fall off during analysis.

  -- Turn the filter over (face down) and place it into the holder base. Center the punch in holder base opening.

  -- In a similar manner, place a second Mylar square over the filter punch. Although the two Mylar sheets are not electrostatically attracted to one another, they are attracted to most other objects, including tweezers, fingers, sample holder bases, and the tissue paper. Some caution is necessary to insure both Mylar squares are lying flat.

  -- Place the retainer ring over the filter, squeeze it slightly to reduce its circumference, and place it over the filter to hold it flat. Note: the bottom Mylar sheet and the filter must be completely flat against the inner lip of the holder bases: the x-ray signal is sensitive to distance travelled, and slight changes in the distance between the x-ray tube, the filter, and the detector will have measurable effects. The bottom Mylar must be as free as possible of wrinkles. Careful tension on alternate corners of the Mylar will generally remove residual wrinkles. Caution: take care that the retainer ring does not pop out as tension is applied to the Mylar.

  -- Proceed in a similar manner for the remaining samples.

  -- After all sample are loaded, double check that the sample ID on the Logsheet matches the ID on the empty PetriSlide for each position.

-- If samples will not be loaded immediately into the XRF sample chamber, place a large, clean Kimwipe over the holders and place the Analysis Logsheet on top.

-- Proceed to Section 4.3.3.

4.3.3 Loading the Analyzer

The following steps transfer the loaded sample holders into the XRF sample chamber:

- For sample that have not been loaded immediately prior to this step, double check the XRF Analysis Logsheet sample positions and IDs against the holder numbers and petri dish/PetriSlide labels.

- If necessary, ramp the x-ray tube voltage and current to 10 kV and 0.20 mA, respectively, using the procedure outlined in Section 4.2.2.

- Press the red reset button to turn off the x-ray tube. When the tube voltage reads 0.0 kV, move the Air Flow switch to "vent" if necessary (pausing momentarily in the middle "isolate" position) and allow the sample chamber to reach ambient pressure. Double check that x-rays are off as in Section 4.2.3.

- Make sure there are no loose pens, jewelry, etc. on clothing or in pockets that may fall out. Carefully open the analysis chamber cover and make sure it latches.

- If samples are currently in the sample carousel, carefully check that all the sample holder numbers match the sample position numbers stamped on the carousel. Remove the existing samples in the carousel one at a time and in order and place on their original Kimwipe in the correct holder position. Cover with a large Kimwipe.

- Place the new sample holders into their corresponding positions in the sample carousel. Avoid as much as possible letting the holders drop into position; try to ease the samples into position carefully and with a minimum of jarring. As described in Section 2.1.2, do not move any holders through the air space immediately above the QA sample.

- Double check the holder numbers against the carousel positions before closing the sample chamber cover. Close the cover by releasing the latch at the rear of the chamber and slowly lowering the lid.

- Move the Air Flow switch to the "vacuum" position, pausing briefly in the middle "isolate" position, to begin evacuating the sample chamber. Note: this step should be performed before the x-ray tube is energized, as often the sample chamber cover will settle slightly as the vacuum is created, tripping the safety interlock on the cover and turning off the x-ray tube anyway.

- Turn on the x-ray tube voltage tube and current by pressing the kV and mA buttons and pressing **<Enter>** after each (the previous values of 10 kV and 0.20 mA are retained by the system and will appear in the numeric keypad display as default entries). Note: the x-ray tube should not be left off longer than necessary.

- Move the Mode switch to the "Auto" position.

- Cover the Kimwipe on which the petri dishes or PetriSlides are sitting with another large Kimwipe.

- Place the XRF Analysis Logsheet for the samples just loaded beside the 8000 monitor.

4.3.4 Starting the Analysis

The analysis run is initiated by the following steps:

- Checking Library Space

  -- Place the current program disk in drive 0 (if not already in place) and the current data disk in drive 1 (the numbers of the current program and data disks are recorded on the shelf where the disks are stored). Close the drive doors by pushing to the right until they latch. The green "ready" light will illuminate after 3-5 seconds.

  -- Check that enough space exits in the library for another run. Libraries typically hold spectra and associated files for four full analysis runs. Check the XRF Analyzer Logbook (Figure 2-8) for the number of runs already saved to the desired library.

  -- If a number of small runs have been saved to a given library and the amount of storage space in the library is in question, at the "*" prompt type the following:

  LIB/AS 1=DL1:xxxxxx (or, **LIB/AS 1=DL1:xxxxxx.KVX**)
  LIB/NAM 1

  The first command assigns logical device 1 to the xxxxxx.KVX library in drive 1. The second command lists the NAME files contained in the xxxxxx.KVX library. The resulting display is similar to Figure 4-12. The bottom of the display indicates the amount of disk space available for spectra files. Because each filter analyzed results in 5 spectra files, the number of filters which may be saved to the library may be estimated. A full run of 16 samples (including QA standard) saves 80 spectra files. Note, however, that such numbers are estimates only, as several other files are created during an analysis run as well (e.g., NAME file, U3 files). Furthermore, the number of files which may be saved in a library is usually limited first by the number of directory entries (maximum 243), which must include spectra file names, NAME files, U3 files, blank spectra created by the MAKE_BLANK program, etc. If in

doubt as to whether another run can be completely saved to a library, err on the side of caution and create a new library.

- Creating New Library

  If a new library is required, follow the following steps:

  -- Type **EX/EX <Return>** (EXit/EXternal) at the "*" prompt to shell to the TSX operating system ("." prompt).

  -- Type **DIR DL1: <Return>** to obtain a directory listing of the libraries on the data disk in drive 1.

  -- At least 2500 blocks are required for a new library. If the disk is full, refer to Section 4.3.4.3 to format and initialize a new disk. If 2500 blocks are free, create a new library by typing:

  COPY/SETDATE FILTER.KVX DL1:xxxxxx.KVX <Return>,

  where xxxxxx.KVX is the new library name (maximum six characters). The convention for library names is that the first 2 to 4 characters are used for the project identifier, and the last 2 characters are reserved for the library number (e.g., CARB1.KVX, DV14.KVX).

```
.DIR DL1:
 13-Dec-89
HAW5  .KVX  2500P 06-Dec-89      HAW6  .KVX 2500P 08-Dec-89
BULL1 .KVX  2500P 12-Dec-89
 3 Files, 7500 Blocks
 12882 Free blocks
```

Figure 4-12. Example of TSX Directory Listing.

Miscellaneous small projects which do not warrant a separate library are placed in a MISCx.KVX library, where x is a number starting with 1. The **SETDATE** command switch insures that the current date is applied to the new library.

-- Type **DIR DL1: <Return>** to verify that the new library was created on the data disk.

-- Remove the data disk by pressing the small black button to the left of the drive door. After a short pause the drive door will pop open and the disk may be removed. With a ballpoint pen, write the new library name and its creation date on the label. Replace the disk in the drive and close the door.

-- Type **OFF <Return>** to return to the Toolbox "*" prompt.

• Formatting and Initializing New Disk

If a new data disk is required, follow these steps to format and initialize a new disk:

-- Obtain a new disk from the box under the work table. Place the large disk label in the label indent in the front of the disk, and a small edge label on the end of the disk.

-- Obtain from the "Kevex Disk Logbook" (Figure 2-12) the next disk number. Record this number on the large and small labels on the disk.

-- Make an entry in the "Kevex Disk Logbook" for the new disk, including: the disk number; location (while the disk is used, its location is "XRF ROOM"; when it is archived, its location is "Archive"); operator's initials; and intended use (data disk, backup disk, or replacement program disk). Note that data disks and backup disks are numbered sequentially and independently of each other and of the disk number.

-- Remove the disk in drive 1 and replace it with the new disk.

-- At the "*" prompt, type **LIB/AS 1=PROG <Return>** (or, **LIB/AS 1=DL0:PROG.KVX <Return>**) to reassign logical device 1 to the PROG.KVX library in drive 0. This is necessary as the disk initialization command will not operate on a drive to which logical drive assignments are still in effect.

-- Similarly, reassign logical device 1 to PROG.KVX on the remote terminal by typing **LIB/AS 1=PROG <Return>**.

-- Type **EX/EX <Return>** (EXit/EXternal) to shell to the TSX operating system ("." prompt).

-- Type **RUN/S/IO FORMIO <Return>**. This command runs a low-level formatting routine on the disk in drive 1. Formatting begins

immediately with no further warning, so be sure the disk in drive 1 is the new disk and not a previously used data or backup disk.

-- When the "." prompt reappears, type **INIT/BAD DL1: <Return>**. This command initializes the directory area of the disk while checking for bad disk blocks. Double check that the **DL1:** portion of the command is present to avoid erasing the directory of the program disk in drive 0 (the default drive if **DL1:** is not specified). After asking several confirmation questions, the program will proceed to initialize the disk.

-- When the "." prompt reappears, type **DIR DL1: <Return>** to insure that the disk is operational. The expected response indicates that no files exists on drive 1 and reports the number of free blocks on the disk.

-- Type **OFF <Return>** to return to the Toolbox "*" prompt.

-- Place the empty disk sleeve on right side of the current disks stored next to the 8000 terminal. Update the list of current disk numbers to include the new disk.

-- Follow the steps in Section 4.3.4.1 to create a new library on the new disk.

• Starting the Analysis Program

-- Check the printer paper supply to insure at least five pages remain. Check the printer ribbon for possible replacement. Make sure the top of the paper is adjusted to the edge of the plastic cover. Finally, insure that the printer is on-line.

-- At the Toolbox prompt ("*"), type **RUN FILTER <Return>** for normal Teflon membrane filters or **RUN FILTER-GF <Return>** for glass fiber or quartz filters (the only difference between the two programs is the tube current setting for conditions 1,2 and 5, which is adjusted downward in FILTER-GF to reduce the amount of detector deadtime, in turn due to the amount of x-ray backscatter from the thicker glass fiber and quartz filter media).

-- The program will ask for the data library name. Type the desired library name. The program will automatically add "DL1:" as a prefix and ".KVX" as a suffix to the user-supplied name; do not include these as part of the library name.

-- The program will assign logical device 1 to the library specified and display a listing of the NAME files in the library. If the specified library is not found on drive 1, Toolbox does not report an error; instead, it retains the previous library assignment to logical device 1. Watch the NAME file listing closely to insure the desired library name is displayed at the top of the screen (note: the library name is quickly overwritten, so the operator must be alert). If the library

displayed is incorrect, abort the program by pressing **<Ctrl><A>** (**^A**, for Abort).

-- After a brief pause, the NAME file listing is erased and a checklist appears on the screen (Figure 4-13).

-- Proceed through each item on the checklist, moving the cursor down one item at a time by using the down-arrow cursor key at the top of the keyboard (refer to the keyboard diagram in Figure 2-5). Do not hit **<Return>** until the end of the checklist is reached. As a safety precaution, if **<Return>** is pressed before the cursor has reached the bottom of the checklist, the program will not continue and the cursor will return to the top of the screen. The following notes supply additional information for items on the checklist:

- Sample IDs are entered by pressing the **<Setup>** firmware key, followed by option 1 at the first menu and option 2 at the second menu. A screen is displayed for sample positions 0 through 15 (Figure 4-14). Sample IDs are typed from the

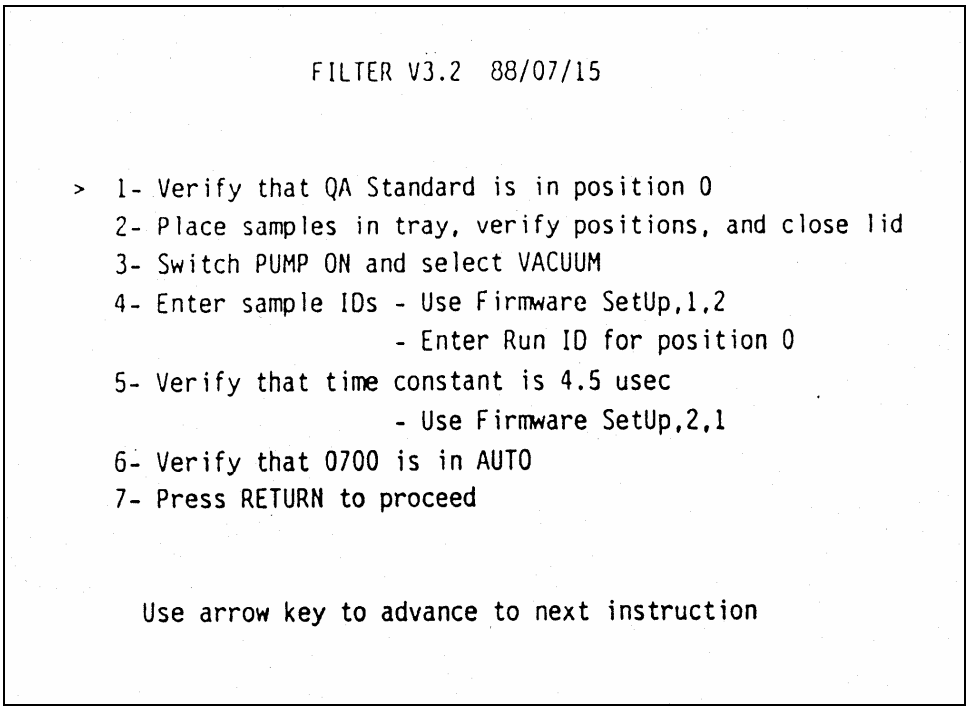


Figure 4-13. XRF FILTER Program Checklist.

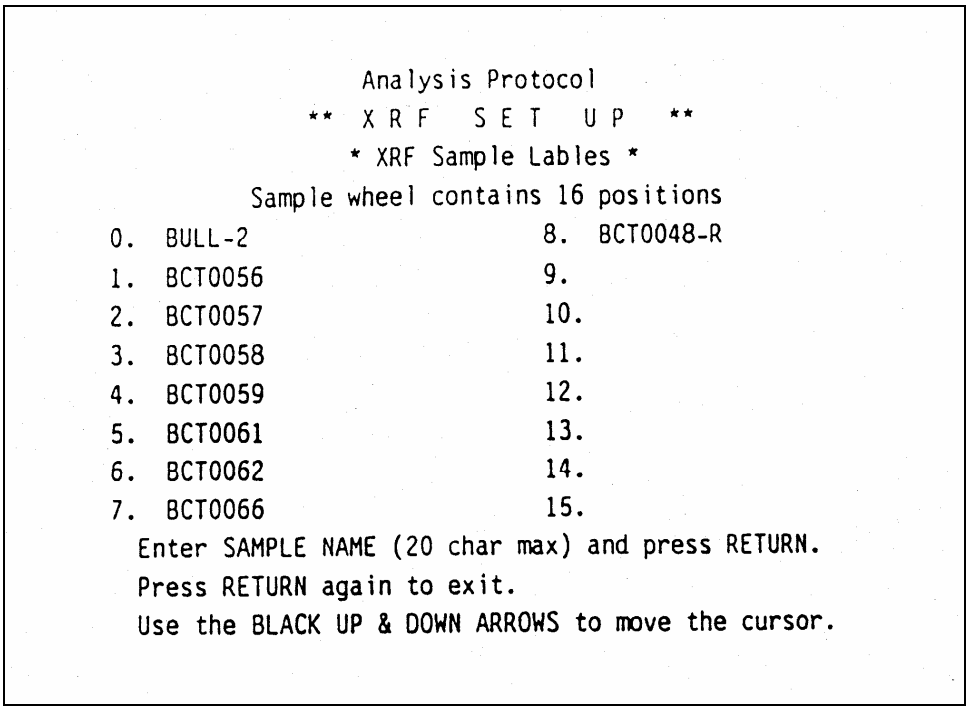


Figure 4-14. Example XRF Sample ID Input Screen.

XRF Analysis Logsheet, including the run ID for position 0. Note that a **<Return>** completes each line, that the up and down cursor keys allow movement between entries, that the **<Del>** key acts as a backspace, and that entries cannot be edited once the **<Return>** is pressed. Incorrect entries are amended by placing the cursor on the appropriate line and retyping the ID in its entirety. For runs containing fewer than 15 samples, extra ID entries from the previous run may be removed by placing the cursor at the beginning of the line and pressing **<Space>** followed by a **<Return>**. When all IDs are entered and verified, a final **<Return>** must be pressed to save the new entries and return to the second menu. From the second menu the **<Setup>** key is pressed again to return to the checklist on the main screen.

- The time constant setting is verified by pressing the **<Setup>** firmware key, followed by option 2 at the first menu and option 2 at the second menu. A screen is display containing various data collection parameters (Figure 4-14). Check that the time constant is 4.5 μs and that the mode is "Live Time". Changes are made to these items by entering the number of the item, followed by a <Return>setting, and another **<Return>**. When both settings are correct, press the **<Setup>** firmware key to return to the main menu.

-- When all items have been checked and the cursor is positioned in front of the last item, press **<Return>** to continue. The program will then ask for the number of samples to be analyzed (excluding the QA standard, which is assumed and not counted). The default entry is 15, which may be accepted by simply pressing **<Return>**. If the run contains fewer samples, enter the number followed by a **<Return>**.

-- A new screen will appear with three analysis protocols (Figure 4-15). The cursor will appear next to Protocol A, the default entry. Refer to the XRF Analysis List (Figure 2-7) for the correct protocol

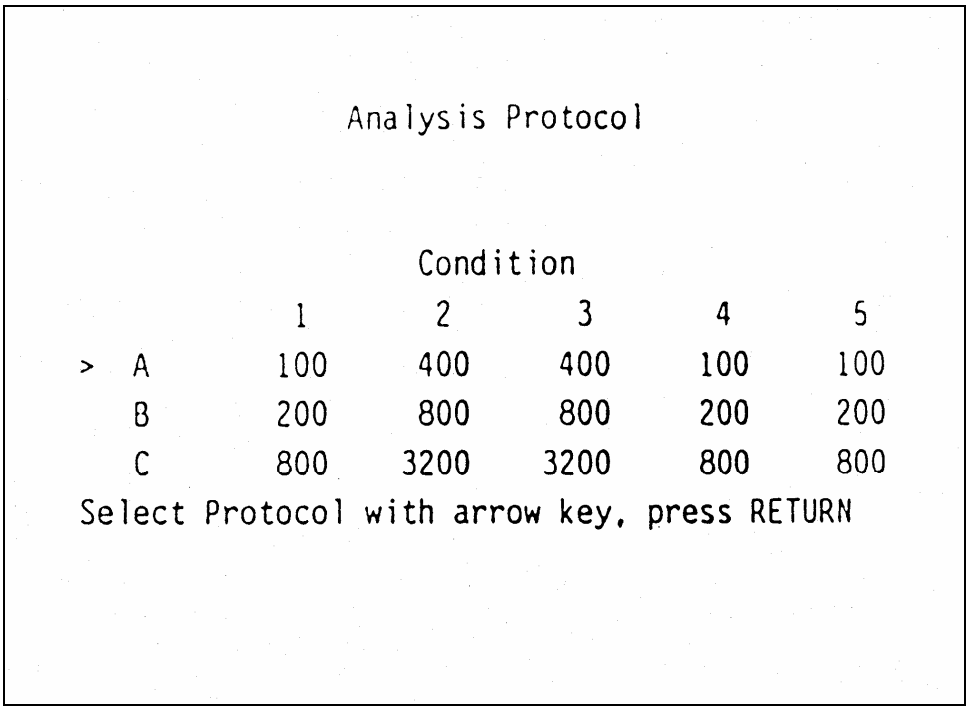


Figure 4-15. XRF FILTER Program Analysis Protocol Menu.

for the project being analyzed. Position the cursor beside the desired protocol. Press **<Return>** to select the protocol and begin the analysis run.

-- Add an entry to the XRF Analyzer Logbook for the run as shown in Figure 2-10, including date, operator's initials, analysis run ID, library name, and disk number. Similarly, complete the analysis section of the XRF Analysis Logsheet (Figure 2-9).

-- After approximately 1 minute, the program will print a listing of the analysis protocol and IDs. Double check the IDs printed against the Analysis Logsheet. Note any errors on the Logsheet. Note: if the printer is off-line or has no paper, the program will simply wait for the printer to become ready, essentially "hanging" the program. If a listing does not appear, check the printer again to insure it is operational.

-- After the sample listing is generated, the program will begin ramping the x-ray tube voltage and current to condition 1 settings. Watch the x-ray tube voltage display for changing values to insure that the program is running correctly and communicating correctly with the 0700 x-ray cabinet. Note: communication between the 8000 terminal and the 0700 x-ray cabinet is one-way only; no handshaking signals are exchanged to insure the x-ray tube, filter bar, secondary target wheel, and sample carousel are actually doing what the program is telling them to do. The most frequent cause of a lack of response at the x-ray cabinet is the mode switch being in the "manual" position, which locks out commands from the 8000 terminal.

-- The operator must insure that the program is running properly before leaving the room (i.e., make sure the sample listing is printed and the x-ray tube voltage is ramping up). If the program is not proceeding normally, press **<Ctrl><A>** (**^A**, for Abort) and restart the program again. Note: Toolbox does not copy over files with the same file names; instead, a new version is created. The version numbers are maintained and reported in the directory listings. If a program is aborted and restarted, the operator will later find several versions of the NAME files for that run.

-- After the x-ray tube voltage and current are ramped to their initial values, the program allows the x-ray tube to stabilize for a period of time before beginning to collect data. The operator must check the analyzer after approximately 15 minutes have elapsed to insure the program is collecting data (i.e., a spectra appears on the screen and is dynamically updating). This check is particularly important before the operator leaves at night.

-- The screen intensities on both the 8000 and remote terminal displays should be turned down at night to avoid "phosphor burn".

4.3.5 Completing the Analysis

As data is collected, a spectra appears on the display (Figure 4-16) which is constantly updated until the Live Time reaches the Preset Time (displayed in the upper right corner of the screen). At that time, the spectral data is saved, the sample carousel is advanced to the next position, the screen clears, and a new spectrum is collected. After the 16th sample position is analyzed, the program changes the x-ray tube voltage and current, the filter bar, and the secondary target wheel to the next analysis condition parameters. After the x-ray tube stabilizes at these new conditions, the sample carousel again advances through the 16 sample positions. This cycle continues through the 5 analysis conditions.

At the end of the complete analysis run, the x-ray tube is ramped to 40 kV and 0.80 mA (tube idle conditions) and the filter bar, secondary target wheel, and sample carousel are returned to their home positions. The program creates U3 files for each of the samples in the data library, and suspends the program until the operator returns.

When the samples are ready to be unloaded, press **<Return>** to allow the program to continue. The x-ray tube will be ramped to 10 kV and 0.20 mA in preparation for removing the analyzed samples and loading new samples.

4.3.6 Filter Unloading

After the program is finished (the "*" prompt reappears) and the x-ray tube is set to 10 kV and 0.20 mA, turn the Air Flow switch to the "vent" position, pausing momentarily in the middle

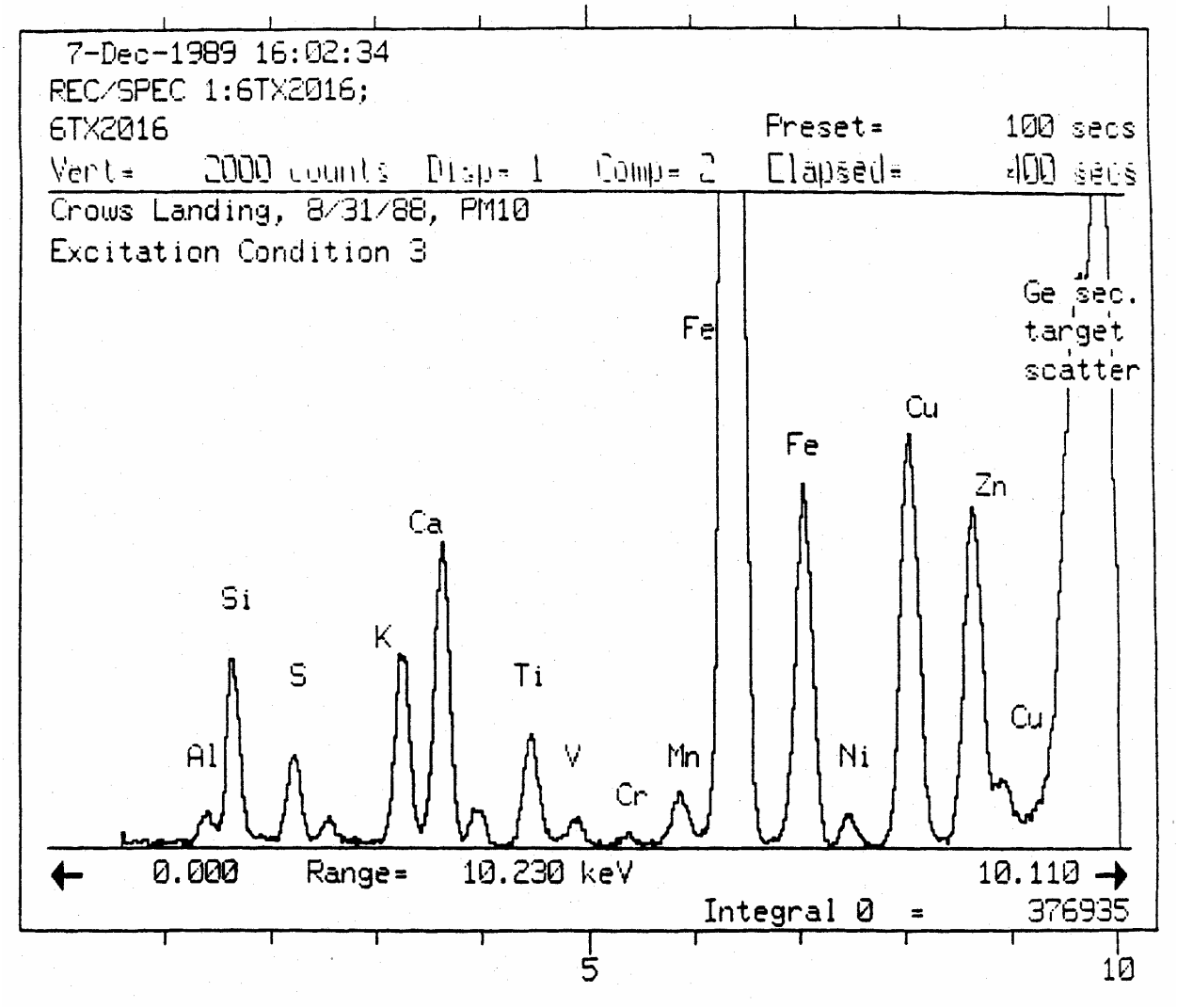


Figure 4-16. Example XRF Spectrum, Condition 3.

"isolate" position. While the sample chamber slowly returns to ambient pressure, remove the large Kimwipe covering the petri dishes or PetriSlides for the samples. Press the red reset button to turn off the x-ray tube. Note: occasionally when the Air Flow switch is moved from one position to another the x-ray tube power circuit will trip itself and turn off power to the tube; this is reflected in the tube voltage display dropping to 0.0 kV. If this occurs, press the red reset button anyway to reset the control circuitry. The following steps outline unloading the filters:

- Check that the x-rays are off as in section 4.2.3.
- When the sample chamber reaches ambient pressure (the hissing sound ceases), open the sample chamber cover until it latches.
- Compare the holder numbers to the sample position numbers on the carousel wheel.
- Remove each holder one at a time and in order, returning it to the appropriate place on the Kimwipe next to its petri dish or PetriSlide. Take care that none of the holders passes over the QA standard/detector area as they are unloaded.
- Load the next set of samples if another set of samples is ready for analysis (refer to Section 4.3.3). Close the chamber cover by pulling the bottom of the latch at the back of the chamber and slowly lowering the cover until it has settled on the o-ring seal.
- Move the Air Flow switch to the "vacuum" position, pausing momentarily in the "isolate" position. Press the kV button and **<Return>** to return the x-ray tube to 10 kV; press the mA button and **<Return>** to return the x-ray tube to 0.20 mA.
- If another run was loaded, check that all files necessary for processing the run just completed are in its library (see Section 5.2) and start the next run following the procedures in Section 4.3.4.
- Compare the sample holder numbers and petri dish or PetriSlide ID numbers to the entries on the XRF Analysis Logsheet.
- Remove the retainer ring from the first holder by pinching it slightly to reduce its circumference and set it aside.
- Open the petri dish or PetriSlide and invert the sample holder over it, allowing the filter to slide into the container. Replace the lid.
- Similarly, unload the remaining samples.
- Record the unloading date and operator's initials on the XRF Analysis Logsheet (Figure 2-9).

- Remove the two-page printout from the printer and place it behind the XRF Analysis Logsheet.

- Place the samples in a new shelf position in the XRF sample cabinet; label the new stack of samples with the project name and the notation "Analyzed".

- Place the XRF Analysis Logsheet by the remote terminal for further processing (Section 5.2).

- Stack the empty holders and retainer rings on a Kimwipe, cover with a second Kimwipe, and set aside.

- Remove the Kimwipe on which the samples were loaded. Insure that all remnants of tape holding the Kimwipe in place are removed from the table.

4.4 Analyzer Shut-Down

The XRF analyzer is generally left running at all times. The x-ray tube should be set to 40 kV and 0.80 mA (tube idle conditions) when not in immediate use. Disks should be removed from the drives if the analyzer is not used for more than four hours. The screen intensities on both the 8000 and remote terminal (IBM-XT) displays should be turned down when the terminals are not in use or when left overnight to avoid "phosphor burn".

The XRF Supervisor may decide to turn the system off during electrical storms or during other situations where electrical damage to the system is likely. The following steps should be followed when turning the system off:

- The x-ray tube is ramped to 10 kV and 0.20 mA.

- The red reset button is pressed to turn off the x-ray tube.

- The Air Flow switch is moved to the "vent" position, pausing momentarily in the "isolate" position.

- Remove any samples which are still in the sample chamber. The QA standard is left in position 0.

- The vacuum pump switch is moved to the "off" position.

- The power control key is turned to "off" position.

- Both disks are removed from the disk drives and placed in their appropriate sleeves on the disk storage shelf.

- The power control switch on the top of the disk drive unit is turned to its "off" position.

- The Crosstalk communications program on the remote terminal is terminated by pressing **<Esc>**, followed by typing **QUIT <Return>**. At the "C>" prompt, the IBM XT may be turned off.

5.0 QUANTIFICATION

5.1 Calibration procedures

Calibration of the XRF analyzer is achieved by analyzing μMatter thin film standards for all elements of interest between Na and Pb. These standards are vacuum deposited elements or salts on 37 mm Nuclepore filters. The standards are stored in PetriSlides, deposit sides up, in a locked sample freezer to retard oxidation and aging. These samples are loaded carefully into 37 mm holders using the procedures outlined in Section 4.2 and analyzed using the FILTER program under Protocol A. Two to four Nuclepore blanks are analyzed in the first run for use in blank subtraction (see Section 5.2).

After analysis of the standards, instrumental response in counts per second per $\mu g/cm^2$ (x-ray count rate normalized to concentration) for each element is calculated from printouts of the *.RAW files for the calibration runs. These calibration coefficients are entered into the file CALCOEFF.DAT by running program CALCOEFF.EXE. The calibration coefficients stored in file CALCOEFF.DAT are read by program PRXRF during processing of sample data.

Calibrations are performed at DRI every 3 months or when results from the QA standard which is analyzed in every run consistently falls outside the ±5% intervals.

Peak overlap correction factors are calculated from the same calibration run printouts of the *.RAW files. For each peak overlap (print file OVERLAP.DAT for a listing of all peak overlaps), calculate the correction factor as

$$O_{ij} = N_i / N_j$$

where O_{ij} = overlap of element j on element i
N_i = net counts for element i when analyzing standard of pure element j
N_j = net counts for element j when analyzing standard of pure element j

Enter the overlap correction factors into file OVERLAP.DAT by running program OVERLAP.EXE. Also enter correction factor uncertainties, using 10% uncertainty for interference from $K_ß$, L and M lines, and 20% for interference from $K_α$ peak tails. Overlap correction factors need to be calculated only once per year, or when a change in the detector resolution is noticed.

5.2 Calculations

Data processing flow is depicted in Figure 5-1. Basically the steps involve creating an average blank spectrum for each condition, performing the blank subtraction and making

escape peak corrections to yield net counts, transferring the net counts to an IBM-compatible file, calculating μg/cm^2 and μg/filter values, and reporting the data. The following sections will describe each of these steps in more detail.

5.2.1 Development of Blank Spectra

When the sample analysis lists are organized, lab blanks appropriate for the samples to be analyzed are located and included. Between 2 and 5 filters should be analyzed from each filter lot if possible, particularly if the filters are glass fiber or quartz or if the filters are from a manufacturer known to have high levels of contaminants or large background variabilities. The lab blanks should be analyzed in the first run for a given project, so as to allow the blank spectra to be developed and the subsequent calculations to proceed.

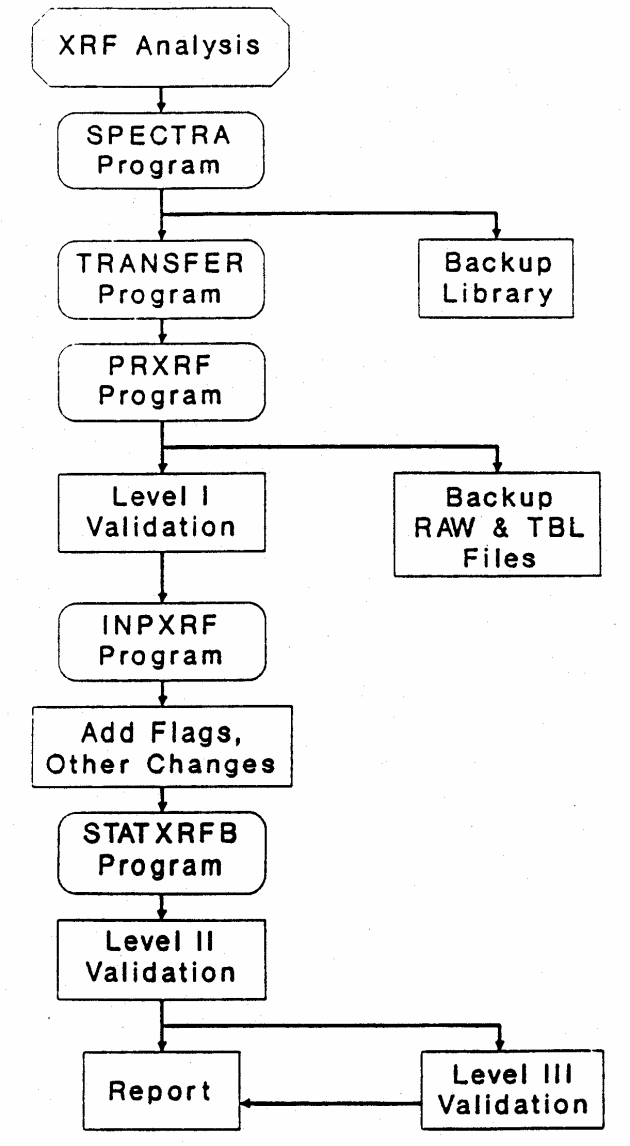


Figure 5-1. Flow diagram of XRF Data Processing.

Blank spectra are created as simple averages of the lab blank spectra for each condition, with corrections for escape peaks on conditions 4 and 5. These spectra are created by the MAKE_BLANK program as follows:

- Insure that the data disk containing the appropriate library is placed in drive 1 and that the current program disk is placed in drive 0.

- Insure that the printer has at least 10 sheets of paper remaining, that the printer ribbon is in good shape, and that the printer is on-line.

- At the "*" prompt type **RUN MAKE_BLANK <Return>** to begin the program.

- The program will ask for the library name. Type the library name without a "DL1:" prefix and without a "KVX" suffix.

- The program will display the NAME file listing for the library specified. Check the top of the display quickly to insure
the intended library has been assigned to logical device 1. If the library is incorrect, pres **<Ctrl><A>** (**^A**) to abort the program and restart it.

- After a brief pause, the screen will clear and the operator will be asked for the number of spectra to be averaged. Type the appropriate number, followed by a **<Return>**.

- The program will then ask for sample IDs to be entered and that the display be set to a log scale. Ignore the request for a log scale. Insure that the automatic vertical scaling option is active (the red light above the **<AutoVS>** firmware key is illuminated); press the **<AutoVS>** firmware key if necessary to activate the option. Also, insure that the horizontal scale is fully compressed by pressing the firmware key labeled ">><<" several times.

- Enter the lab blank IDs by pressing the **<Setup>** firmware key, followed by option 1 at the first menu and option 2 at the second menu. The screen listing sample IDs will appear and may be edited as described in Section 4.3.4.4. Note: if the MAKE-BLANK program is run immediately after the lab blanks are analyzed, their IDs will already appear on the ID list. Simply remove the extra entries by placing the cursor at the beginning of each line and press **<Spacebar>** followed by a **<Return>**.

- Type the blank spectra ID in position 0. The blank spectra ID is defined in the sample analysis list and is formatted as "BLANK-xxxxxx", where "xxxxxx" represents a 2 to 4 character project identifier followed by a 1 to 2 digit quarter or batch number (e.g., BLANK-SJV3, BLANK-CARB1).

- Press an extra **<Return>** to save the modified ID list and to return to the second menu. Press the **<Setup>** firmware key to return to the main screen.

- Press **<Return>** to allow the program to continue. The rest of the program requires no further operator interaction. Spectra for each condition are recalled, escape peaks subtracted, and averaged into a single spectra. The

program completes by printing the averaged blank spectra for each of the five conditions.

- Record the blank spectra name in the line provided on the XRF Analysis Logsheet. Indicate on the Logsheet that MAKE_BLANK was run, the date, and the operator's initials (Figure 2-9).

- Record the blank spectra name, date created, library name, and disk number at the front of the current XRF Analysis Logbook.

- When the plots of the blank spectra are done printing, remove them from the printer and place them behind the XRF Analysis Logsheet.

5.2.2 Validation of Blank Spectra

The calculated blank spectra must be verified manually for unusual levels of contaminants or other abnormalities. The spectrum for each condition is recalled and examined for unusual peaks or high levels of typically occurring peaks. The examination of the blank spectra must be performed by the XRF Supervisor or Laboratory Supervisor, and they must initial the XRF Analysis Logsheet before processing can continue.

5.2.3 Spectral Processing

The next step in XRF data processing is subtracting the blank spectra from each sample. This converts gross counts in each region corresponding to an element to net counts. The integration region for each element is defined by its starting and ending keV values in a U2 file in the PROG.KVX library on the program disk. The integrated gross and net counts are stored in U3 files which are created at the end of the FILTER or FILTER-GF program. The program which performs these calculations and stores the gross and net counts in the U3 files is typically run from the remote terminal, allowing data processing and data collection on the next run to occur simultaneously.

Before the next run is started, the operator must insure that a copy of the blank spectra exist in the same library as the data to be processed. This is automatically the situation for the first library of a project, as MAKE_BLANK will place the blank spectra in the same library as the spectra for the lab blanks. However, subsequent libraries do not initially contain the blank spectra. Generally, blank spectra should be transferred to a new library immediately after its creation.

- Copying Blank Spectra on Same Data Disk

  The following procedure must be performed from the 8000 terminal, as the remote terminal has only restricted access to the directories of both disks and may not reliably update the directory when the files are copied.

-- Insure the current program disk is placed in drive 0 and the current data disk containing the first and subsequent libraries is placed in drive 1.

-- At the "*" prompt, type **LIB/AS 0=DL1:xxxxxx <Return>** (LIBrary/ASsign logical device 0 to xxxxxx.KVX in drive 1, where xxxxxx.KVX is the first library for the given project.

-- Type **LIB/AS 1=DL1:yyyyyy <Return>** (LIBrary/ASsign logical device 1 to yyyyyy.KVX in drive 1, where yyyyyy.KVX is the new library to which the blank spectra will be copied.

-- Type **LIB/COPY/SPEC/NOQUERY 1:BLANK-zzzzzz.*.*=BLANK-zzzzzz.*.* <Return>** (LIBrary/COPY/SPECtra/NOQUERY all versions and all conditions of BLANK-zzzzzz from logical device 0 (in this case, the first library) to logical device 1 (set to the destination library). Note that the syntax is destination=source. The NOQUERY switch is optional and allows the command to continue without asking for confirmation; otherwise, the terminal will ask for confirmation for each of the five spectra copied.

-- Type **LIB/SPEC 1 <Return>** (LIBrary/SPECtra, logical device 1) to obtain a directory listing of the spectra files in the destination library to insure the blank spectra were successfully copied.

-- Type **LIB/AS 0=PROG <Return>** (LIBrary/ASsign logical device 0 to PROG.KVX library in drive 0) to reset logical device 0 to the program library.

• Copying Blank Spectra on Different Data Disks

When a second or subsequent library exists on a different data disk than the disk with the first library for a given project, the copying process is a bit more complicated. Because the copy command is contained on the program disk, the program disk must remain in drive 0 at all times. This restriction means the spectra to be copied from one data disk to another must be copied first from the original data disk to the program disk, and then copied from the program disk to the second data disk.

The following procedure must be performed from the 8000 terminal, as the remote terminal has only restricted access to the directories of both disks and may not reliably update the directory when the files are copied.

-- Insure the current program disk is placed in drive 0 and the current data disk containing the first library is placed in drive 1.

-- Type **LIB/AS 1=DL1:xxxxxx <Return>** (LIBrary/ASsign logical device 1 to xxxxxx.KVX in drive 1, where xxxxxx.KVX is the library in which the blank spectra were created.

-- Type **LIB/COPY/SPEC/NOQUERY BLANK-zzzzzz.*.*=1:BLANK-zzzzzz.*.* <Return>** (LIBrary/COPY/SPECtra/NOQUERY all versions and all conditions of BLANK-zzzzzz from logical device 1 (in this case, the first library) to logical device 0 (which is PROG.KVX, the library that logical device 0 is normally assigned to). Note that the syntax is destination=source. The NOQUERY switch is optional and allows the command to continue without asking for confirmation; otherwise, the terminal will ask for confirmation for each of the five spectra copied.

-- When the "*" prompt reappears, replace the first data disk with the second data disk. Type **LIB/AS 1=DL1:yyyyyy <Return>** (LIBrary/ASsign logical device 1 to yyyyyy.KVX in drive 1). This command is necessary because logical device 1 is still set to the first library on the first disk. The operating system does not detect that the data disks were switched, and the system will hang if it tries to access the originally assigned library.

-- Type **LIB/COPY/SPEC/NOQUERY 1:BLANK-zzzzzz.*.*=BLANK-zzzzzz.*.* <Return>**. This copies the blank spectra from logical device 0 (the program library on disk 0) to logical device 1 (the new library on disk 1).

-- Type **LIB/SPEC 1 <Return>** (LIBrary/SPECtra, logical device 1) to obtain a directory listing of the spectra files in the destination library to insure the blank spectra were successfully copied.

-- An extra copy of the spectra will now exist in the program library. These may be removed by typing **LIB/DEL/SPEC BLANK-zzzzzz.*.* <Return>** (LIBrary/DELete/SPECtra all versions and conditions of BLANK-zzzzzz on logical device 0, which is PROG.KVX on drive 0). The terminal will ask for confirmation before deleting each of the spectra.

• Processing Spectra

The calculations of gross and net integrated counts for each element is performed on the remote terminal. After insuring the correct data disk is placed in drive 1 and that the blank spectra exists on the desired library, begin processing by:

-- At the "*" prompt on the remote terminal, type **RUN SPECTRA <Return>**. The program will ask for the name of the data library. Enter the drive designation, the library name, and a **<Return>** (e.g., DL1:CARB2, DL1:DV12). Note that the suffix ".KVX" is optional. Unlike the FILTER and FILTER-GF programs, the drive designation is not assumed to be DL1: and is not optional. Note that if typing mistakes are made at the remote terminal, the **<Backspace>** does not work; instead, use **<Ctrl><Backspace>** to erase characters.

-- The screen will clear and the NAME file directory for the selected library will appear. Quickly check the library designation at the top of screen before it is overwritten to insure it is correct.

-- The program will ask for the run ID. Type the run ID from the XRF Analysis LogSheet and press <**Return**>.

-- The program will ask for the name of the blank spectra. Type the name and press <**Return**>. The program will proceed without further operator intervention. The screen at this point will look similar to Figure 5-2.

-- Finally, the program will ask for the number of samples to be processed. Type the number of samples in the run (excluding the QA standard, which is included automatically) and press <**Return**>.

-- Complete the "Spectra" section of the XRF Analysis Logsheet by filling in the date and technician's initials.

The SPECTRA program takes approximately 2 ½ hours to process a full run of 15 samples. However, the speed of operations performed from the remote terminal is dependent upon what the 8000 terminal is doing. If the 8000 terminal is sitting idle, the program on the remote terminal will run slower [sic]. Status messages will appear on the screen periodically so the progress of the program can be monitored.

- Transferring U3 Files

When the SPECTRA program is finished and the "*" prompt reappears, the contents of the U3 files must be transferred to an IBM-compatible file for additional processing. Because the U3 files cannot be transferred directly to the remote terminal, they must first be converted to TSX ASCII analog files, which are then transferred to the IBM XT.

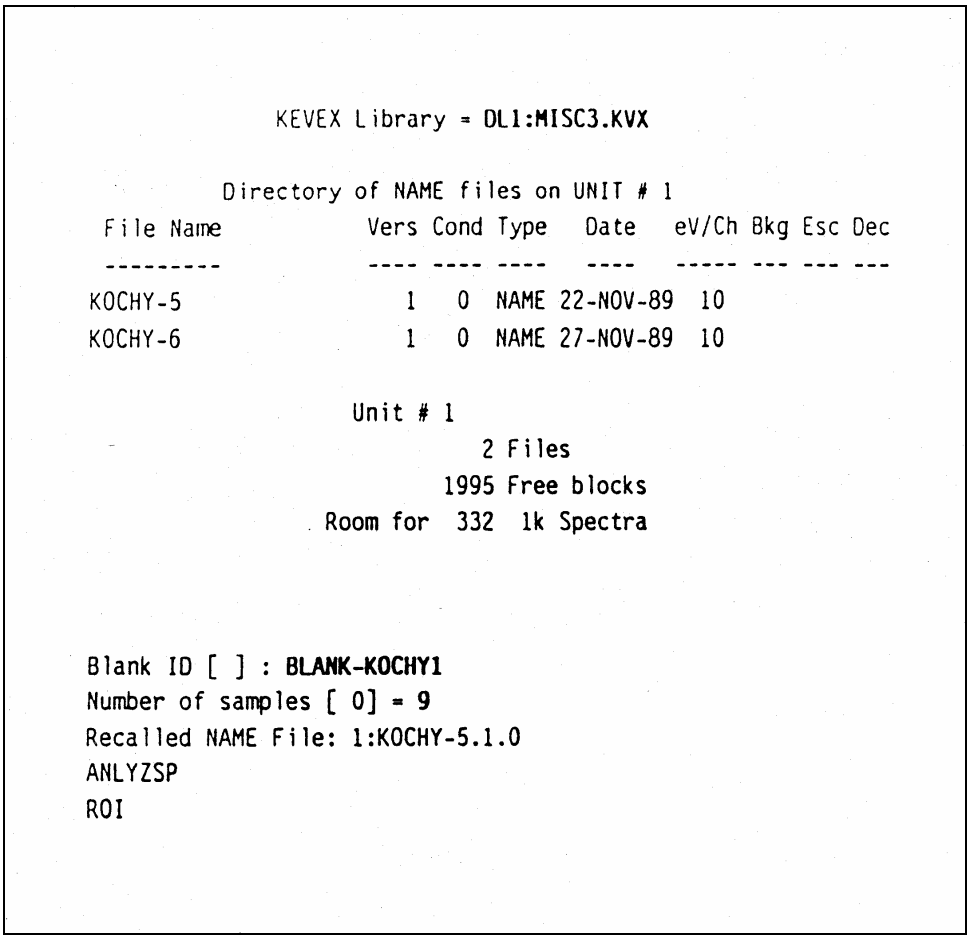


Figure 5-2. Computer Display after SPECTRA Program Started.

-- At the "*" prompt on the remote terminal, type **RUN TRANSFER <Return>**. The program will ask for the name of the data library. Enter the drive designation, the library name, and a **<Return>** (e.g., DL1:CARB2, DL1:DV12). Note that the suffix ".KVX" is optional. Unlike the FILTER and FILTER-GF programs, the drive designation is not assumed to be DL1: and is not optional.

-- The screen will clear and the NAME file directory for the selected library will appear. Quickly check the library designation at the top of screen before it is overwritten to insure it is correct.

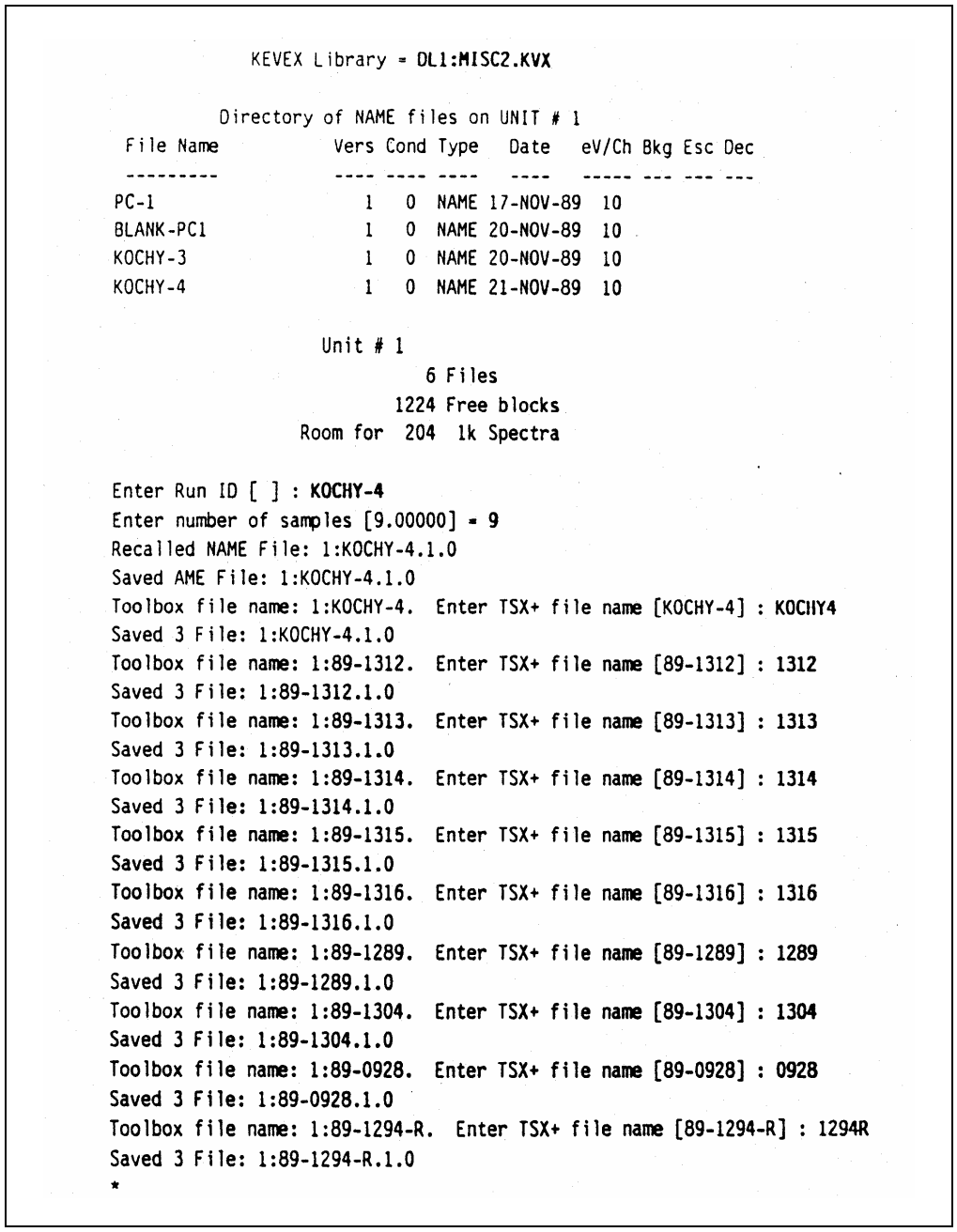
-- The program will ask for the run ID. Type the run ID from the XRF Analysis LogSheet and press **<Return>**.

-- The program will ask for the number of samples to be processed. Type the number of samples in the run (excluding the QA standard, which is included automatically) and press **<Return>**.

-- The program will begin converting the U3 files into TSX ASCII files. As each file is converted, the program will ask for a TSX destination file name. Note that these names must conform to the TSX file naming conventions (i.e., six characters only, no dashes); the extension of ".U3" is added automatically. Because sample IDs frequently exceed six characters in length, type abbreviated six-character file names derived from the sample IDs which will insure each file has a unique name (Figure 5-3). Note that the file names may be typed ahead of the program's prompts for file names, using the XRF Analysis Logsheet as a guide.

-- When the program is finished and the "*" reappears, type **EX/EX <Return>** (EXit/EXternal) to shell to the TSX operating system ("." prompt).

-- Place a formatted 5 ¼" floppy disk with at least 25 K free space in the IBM XT drive. The amount of free space remaining on the disk may be determined by pressing **<Esc>** on the IBM XT keyboard to access Crosstalk's command line at the bottom of the screen (note: if the **<Esc>** key is pressed accidentally at any other time, simply press **<Return>** to exit the



```
            KEVEX Library = DL1:MISC2.KVX

         Directory of NAME files on UNIT # 1
 File Name          Vers Cond Type   Date   eV/Ch Bkg Esc Dec
 ---------          ---- ---- ----   ----   ----- --- --- ---
PC-1                   1    0  NAME 17-NOV-89  10
BLANK-PC1              1    0  NAME 20-NOV-89  10
KOCHY-3                1    0  NAME 20-NOV-89  10
KOCHY-4                1    0  NAME 21-NOV-89  10

                  Unit # 1
                          6 Files
                       1224 Free blocks
                 Room for  204  1k Spectra

Enter Run ID [ ] : KOCHY-4
Enter number of samples [9.00000] = 9
Recalled NAME File: 1:KOCHY-4.1.0
Saved AME File: 1:KOCHY-4.1.0
Toolbox file name: 1:KOCHY-4.  Enter TSX+ file name [KOCHY-4] : KOCHY4
Saved 3 File: 1:KOCHY-4.1.0
Toolbox file name: 1:89-1312.  Enter TSX+ file name [89-1312] : 1312
Saved 3 File: 1:89-1312.1.0
Toolbox file name: 1:89-1313.  Enter TSX+ file name [89-1313] : 1313
Saved 3 File: 1:89-1313.1.0
Toolbox file name: 1:89-1314.  Enter TSX+ file name [89-1314] : 1314
Saved 3 File: 1:89-1314.1.0
Toolbox file name: 1:89-1315.  Enter TSX+ file name [89-1315] : 1315
Saved 3 File: 1:89-1315.1.0
Toolbox file name: 1:89-1316.  Enter TSX+ file name [89-1316] : 1316
Saved 3 File: 1:89-1316.1.0
Toolbox file name: 1:89-1289.  Enter TSX+ file name [89-1289] : 1289
Saved 3 File: 1:89-1289.1.0
Toolbox file name: 1:89-1304.  Enter TSX+ file name [89-1304] : 1304
Saved 3 File: 1:89-1304.1.0
Toolbox file name: 1:89-0928.  Enter TSX+ file name [89-0928] : 0928
Saved 3 File: 1:89-0928.1.0
Toolbox file name: 1:89-1294-R.  Enter TSX+ file name [89-1294-R] : 1294R
Saved 3 File: 1:89-1294-R.1.0
*
```

Figure 5-3. Computer Display during TRANSFER Program.

command line and return to operation as the remote terminal). Type **DIR A:/S <Return>** (directory of a: drive, displaying file sizes) to get a listing of files on the disk along with their sizes and the amount of free space on the disk.

-- On the IBM XT keyboard press **<Esc>** to access CrossTalk's command line at the bottom of the screen. Type **CA A:xxXRFn.RAW <Return>**, where xx is the two-character project identifier and n is a one, two, or three digit run number (e.g., DVXRF23.RAW, SJXRF1.RAW). This command turns on the screen capturing abilities of Crosstalk, capturing everything on the screen to a disk file with the designated name.

-- At the "." prompt, type **TYPE *.NAM <Return>**. This displays the contents of the ASCII name file (only one file, corresponding to the analysis run ID).

-- At the "." prompt, type **TYPE *.U3 <Return>**. This displays the contents of the ASCII representations of the U3 files; files corresponding to each sample on the XRF Analysis Logsheet will be displayed in order.

-- When the "." prompt reappears, press **<Esc>** on the IBM keyboard to access the Crosstalk command line. Type **CA OFF <Return>** to turn off screen capture and to close the file created on the floppy disk.

-- At the "." prompt, type **DEL/NOQUERY *.NAM <Return>** to delete the ASCII name file on the program disk. The NOQUERY switch suppresses a confirmation message before each deletion and is optional.

-- At the "." prompt, type **DEL/NOQUERY *.U3 <Return>** to delete the ASCII files on the program disk corresponding to the U3 files on the data disk. The NOQUERY switch suppresses a confirmation message before each deletion and is optional.

-- When the "." prompt reappears, type **OFF <Return>** to return to the Toolbox operating environment.

-- Remove the floppy disk from the IBM XT and place it with the XRF Analysis Logsheet. Complete the section on the Logsheet titled "Transfer" by filling in the date and the operator's initials.

• Backing Up Library

After a library is full (contains four full analysis runs or the equivalent) and the SPECTRA and TRANSFER programs are run on all runs in the library, the library must be copied to a backup data disk. As discussed in Section 5.2.3.2, the program disk cannot be removed from drive 0 during the copying process, and so the library must be copied first to the program disk in drive 0 and then to the backup disk placed in drive 1:

-- Insure that the current copy of the program disk is in drive 0 and that the data disk containing the desired library is in drive 1.

-- At the "*" prompt, type **EX/EX <Return>** (EXit/EXternal) to shell to the TSX operating system. Because the entire library must be handled as a file to be copied, the TSX operating system is necessary.

-- At the "." prompt, type **COPY DL1:xxxxxx.KVX DL0: <Return>**, where xxxxxx.KVX is the desired library. This command copies the xxxxxx.KVX library from drive 1 to drive 0 while retaining the same name. Note that in this case the destination drive must be specified.

-- When the "." prompt reappears, remove the original data disk and replace it with the current backup disk (the number of which is recorded on the shelf where the disks are stored).

-- At the "." prompt, type **COPY xxxxxx.KVX DL1: <Return>** to copy the library to the backup disk. If a message appears that there is not enough room left on the backup disk, refer to Section 4.3.4.3 on instructions for formatting and initializing a new disk.

-- When the library has been copied and the "." prompt appears, type **DIR DL1: <Return>** to get a directory listing of the files on the backup disk to confirm the library reached its destination. Remove the backup disk, add the library name and the current date to the disk label, and return the disk to its sleeve.

-- Finally, the temporary copy of the library on the program disk must be removed. Type **UNPROTECT xxxxxx.KVX <Return>** to unlock the library in preparation for deletion. Type **DEL xxxxxx.KVX <Return>** to remove the library. Type **DIR *.KVX <Return>** to confirm the library was removed; the directory listing should indicate that at least 2500 blocks are free. Type **OFF** to return to the Toolbox "*" prompt.

-- Record the date and the operator's initials in the Backup section of the XRF Analysis Logsheet for all runs contained in the library.

• Final Calculations

The conversion of background subtracted peak counts to μg/filter for each element takes place on the *.RAW files created by the remote terminal:

-- The disk containing the *.RAW file is taken with the XRF Analysis Logsheet and any other printouts to the Compaq 386 computer located in the wet chemistry lab. Type **C: <Return>** if necessary to set the default drive to the "C >" prompt. Type **CD\XRF <Return>** to change to the XRF subdirectory. If a project subdirectory already exists beneath the XRF subdirectory, type **CD xxxxxxxx <Return>**, where xxxxxxxx is the project name. If the project subdirectory does not already exists, type **MD xxxxxxxx <Return>** (Make

Directory) to create the xxxxxxxx directory and **CD xxxxxxxx <Return>** to change to it.

-- Place the disk containing the *.RAW file into the right 5 ¼" drive and type **COPY B:xxXRFn.RAW <Return>**, where xx is the two-character project identifier and n is a 1 to 3 digit analysis run number. This command copies the xxXRFn.RAW file to the c: drive. Remove the disk from the b: drive and return it to the XRF room.

-- Locate the XRF *.RAW backup disks located next to the computer. These disks are organized as one disk per project. Select the proper disk, or find a new high-density 5 ¼" disk if this is a new project, and place it in the left 5 ¼" drive. Type **COPY xxXRFn.RAW A: <Return>** to copy the file from the c: drive to the a: drive. Restore the disk to its storage location on top the file cabinets.

-- Process the analysis data by typing **..\PRXRF40 <Return>**, (the 40 refers to the latest version, 4.0).

-- The program asks for the project name, two-character project identifier, and the run number (Figure 5-4). From this input the program constructs the xxXRFn.RAW file name and reads data from it.

-- The program then asks for deposit areas and flags for each of the samples analyzed (note: the QA standard is automatically labeled with 1.0 cm^2 and an analysis flag of "q1". The deposit area is found on the XRF Analysis Logsheet, which is in turn taken from the analysis list. Five characters are reserved for the analysis flags, which may include as many as two two-character flags separated by a comma. Typical flags include:

b1	field blank
b2	laboratory blank
f1	filter damaged, outside analysis area
f2	filter damaged, inside analysis area
i	unspecified deposit problems
i1	inhomogeneous filter deposit
i2	deposit smeared or scraped after sampling
i4	foreign objects on deposit surface
q1	routine quality control standard
r1	first replicate analysis

-- The program then reprints the deposit areas and flags input and asks for confirmation of the entries (Figure 5-5). Press **<Y>** if the entries are correct or **<N>** if one or more entries are incorrect; note that **<Return>** is not necessary.

-- The program then displays a match between sample IDs from the NAME file and the *.U3 file names designated during the TRANSFER program. Check each entry to make sure the IDs and data files are properly matched (Figure 5-6). If a discrepancy is

found, notify the XRF Supervisor. If the IDs and file names match correctly, press **<Y>** to initiate calculations.

-- The PRXRF program makes corrections for peak overlaps and peak interferences. It calculates μg/cm^2 and μg/filter values for each of the 40 elements currently reported by DRI. It also flags concentrations for unusual elements which are above their uncertainties

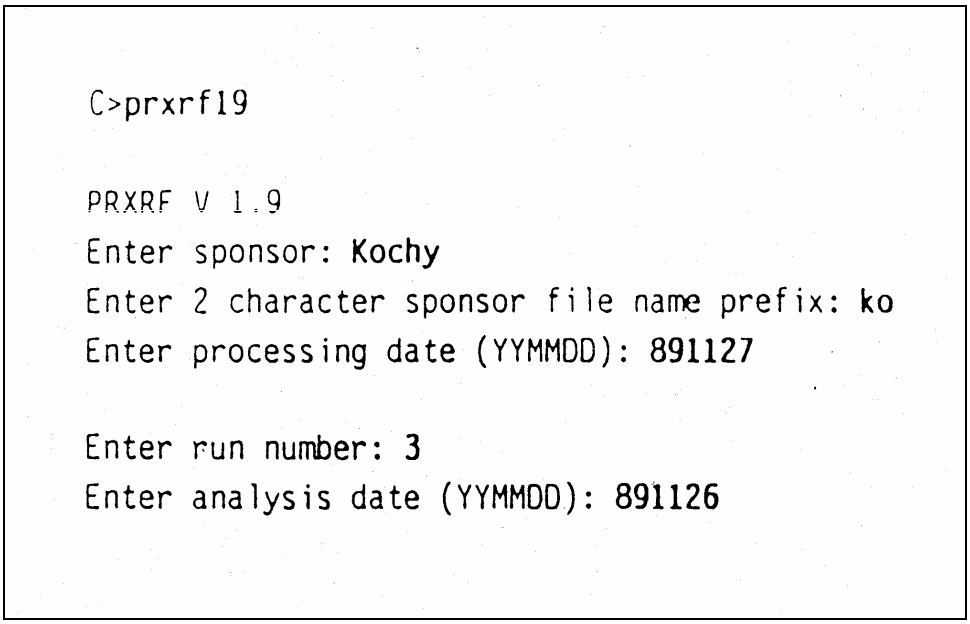


Figure 5-4. Computer Display during PRXRF Program.

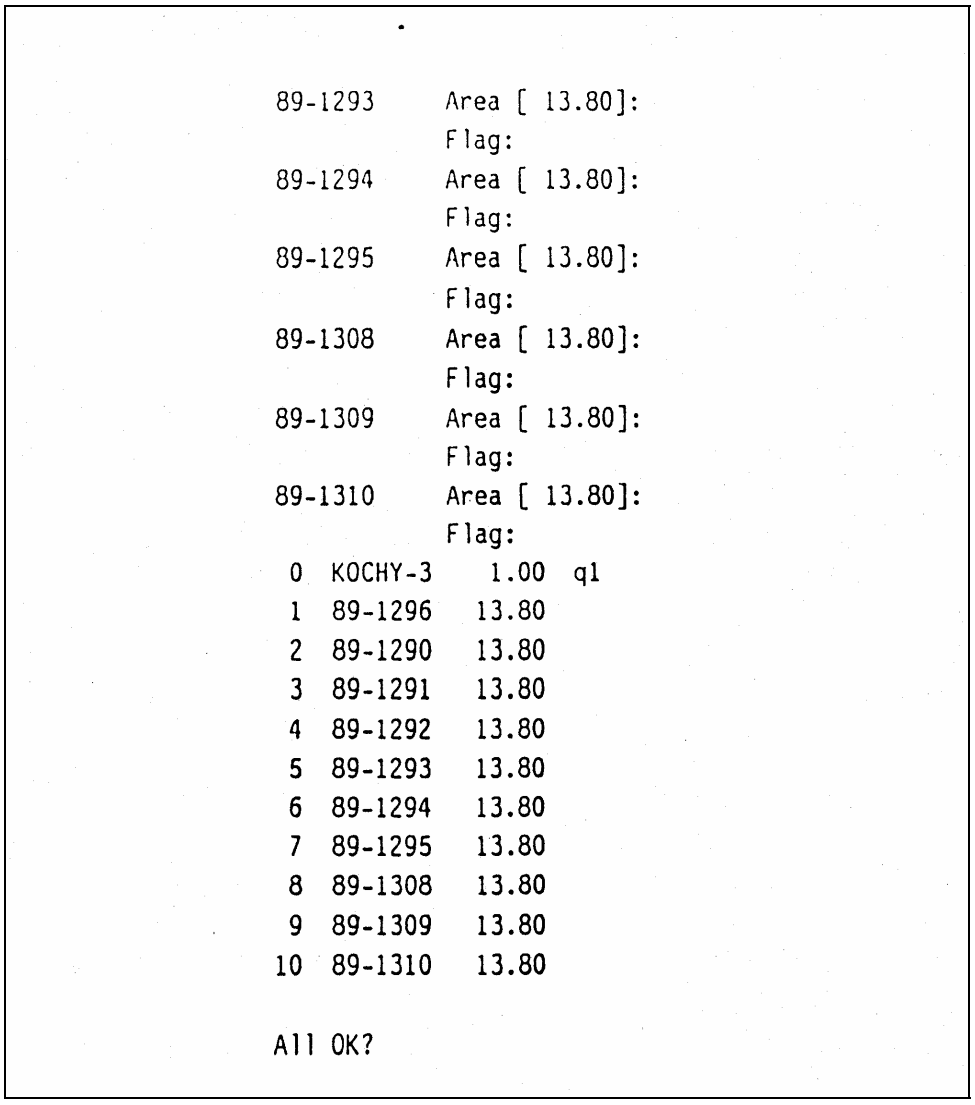


Figure 5-5. First Confirmation Screen of PRXRF Program.

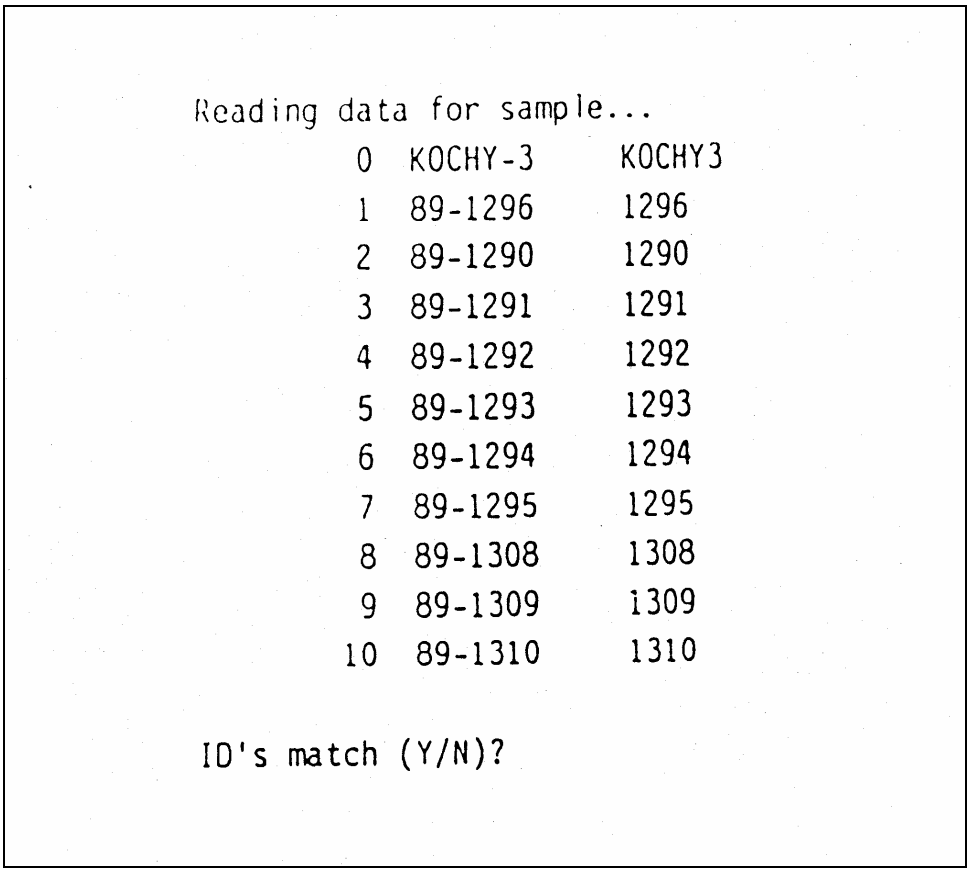


Figure 5-6. Second Confirmation Screen of PRXRF Program.

and elements for which inter-condition concentrations agree poorly.

-- Record the date and operator's initials in the Process section of the XRF Analysis Logsheet.

-- When the calculations are done, the program asks if the operator has additional files to process. Press **<Y>** or **<N>** as appropriate (no **<Return>** is necessary).

-- Two files are created when PRXRF is completed: a file named xxXRF.TBL (where xx is the two-character project identifier), which contains μg/cm^2 data in an ASCII format table; and xxXRF.REC, which contains μg/filter data in an ASCII format for input into a dBase III+ file. When the program is finished and the "C >" prompt appears, type **REN xxXRF.TBL xxXRFn.TBL <Return>** to REName the default tabular output file to a name which includes the run number. If multiple runs were processed in one session of PRXRF, rename the TBL file to reflect the run numbers included (e.g., DVXRF12.TBL includes just run 12, and DVXRF0108.TBL includes runs 1 through 8).

   Do not rename the xxXRF.REC file until all of the current runs have been processed (i.e., until the end of a sampling quarter or of the entire project). At that time rename the xxXRF.REC to xxXn.REC, where n is the range of analysis runs, by typing **REN xxXRF.REC xxXn.REC <Return>** (e.g., REN DVXRF.REC DVX0108.REC).

-- Obtain a printout of the tabular ASCII file by insuring the dot matrix printer to the left of the computer has at least 20 pages of paper left, making sure the printer is on-line, and typing **COPY xxXRFn.TBL PRN <Return>** (Figure 5-7). Remove the printout when it has printed, place it behind the XRF Analysis Logsheet and the other printouts already behind the Logsheet, and place it in a safe place until the library is full and is copied to the backup disk. At that time, record the date and operator's initials in the Backup section of the XRF Analysis Logsheet and deliver the paperwork directly to the XRF Supervisor. DO NOT put the paperwork in the mail slot in the reception area.

DRI X-RAY FLUORESCENCE DATA REPORT
For KOCHY
Run KOCHY-3 analyzed 891120, processed 891127 with program PRXRF V 1.9

Sample ID: KOCHY-3 Deposit Area: 1.00cm2 Sample Flag: q1
Condition 5 Background: 0.82-0.84 0.93-0.95 1.14-1.16 2.52-2.54 KeV

Species	Species Flag	Concentration (ug/cm2) Selected	Cond	Alternate	Cond
Na	l	0.1480 +- 0.4575	5		
Mg	l	-0.0167 +- 0.0881	5		
Al	l	-0.2054 +- 0.0404	5	-2.4898 +- 0.4337	4
Si	l	-8.6395 +- 0.1212	5	-108.8685 +- 1.1828	4
P	l	-0.0574 +- 0.0329	5	-0.6183 +- 0.1599	4
S	m	0.6892 +- 0.0070	5	2.6176 +- 0.0379	4
Cl		0.1693 +- 0.0099	4		
K		0.2921 +- 0.0137	4	0.2762 +- 0.0153	3
Ca		2.4547 +- 0.0254	4	2.2489 +- 0.0300	3
Ti		0.0275 +- 0.0090	3		
V	l	0.0079 +- 0.0118	3		
Cr		0.0241 +- 0.0019	3		
Mn	l	-0.0056 +- 0.0096	3		
Fe	m	3.4166 +- 0.0111	3	2.2528 +- 0.0136	2
Co	l	-0.0080 +- 0.0504	3	-0.0021 +- 0.0346	2
Ni	l	0.0022 +- 0.0027	3	0.0066 +- 0.0016	2
Cu		0.1067 +- 0.0017	3	0.0955 +- 0.0024	2
Zn	l	-0.0112 +- 0.0033	3	0.0044 +- 0.0013	2
Ga	u	0.0581 +- 0.0017	2		
As	l	-0.0007 +- 0.0040	2		
Se	u	0.0068 +- 0.0007	2		
Br		0.0079 +- 0.0007	2		
Rb	l	-0.0008 +- 0.0020	2		
Sr	l	-0.0001 +- 0.0025	2		
Y	l	0.0000 +- 0.0028	2		
Zr		0.0425 +- 0.0016	2		
Mo	l	-0.0100 +- 0.0067	2		
Pd	l	0.0082 +- 0.0106	1		
Ag	l	0.0061 +- 0.0123	1		
Cd	l	0.0090 +- 0.0129	1		
In	u	0.0228 +- 0.0054	1		
Sn	u	1.2704 +- 0.0188	1		
Sb	l	-0.0288 +- 0.0258	1		
Ba	l	-0.0528 +- 0.0836	1		
La	l	-0.0948 +- 0.0913	1		
Au	u	0.0453 +- 0.0022	2		
Hg	u	0.0091 +- 0.0017	2		
Tl	l	-0.0131 +- 0.0058	2		
Pb		0.0082 +- 0.0019	2		
U	l	-0.0007 +- 0.0047	2		

Figure 5-7. Example of Tabular Printout from PRXRF Program.

6.0 QUALITY CONTROL

Quality control for the XRF analyzer consists of checking the performance of the analyzer against a QA standard which is analyzed in every run and looking at replicate analyses.

6.1 Performance Testing

The PRXRF program adds data from the QA standard in position 0 to a file named STD.RQA in the \XRF subdirectory. This data must be examined to insure the XRF analyzer is performing correctly. Immediately after the PRXRF program is run and the printout of xxXRFn.TBL is obtained, type **..\SHOWQA <Return>**. At the program's prompt for a file name, input the full file name of the xxXRFn.RAW file.

The SHOWQA program displays the gross counts for four elements in the multi-element QA standard, including tin (Sn) under condition 1, iron (Fe) under conditions 2 and 3, calcium (Ca) under conditions 3 and 4, and silicon (Si) under condition 5 (Figure 6-1). These values are recorded on the XRF Analysis Logsheet (Figure 2-9) and compared to the ranges printed on the Analysis Logsheet. The ranges correspond to ±3% intervals from the historical mean for each element and condition. These intervals are considered to be warning limits. The actual criterion for the QA standard is ±5%; gross counts outside the ±5% interval requires immediate notification of the XRF Supervisor. Any values which are outside the ±3% limits are highlighted. If all values are within ±3% the line labeled "chk" is marked "ok" followed by the operator's initials.

The SHOWQA program actually reports gross counts for all the samples in the analysis run on two screens; press any key to display the second screen. At the next file name prompt, a new file name may be entered or the program may be ended by pressing **<Return>**.

6.2 Reproducibility Testing

Replicates of analyzed samples are performed at the rate of 10%. This corresponds to one or two replicate per analysis run after the first run. The general pattern to be followed is one run with two replicates, followed by two runs with one replicate each. This generally corrects for the changing number of original samples which can be analyzed in each run due to the number of replicates. The total number of replicates is compared to the total number of filters prior to the last run for a given project, and additional replicates are placed in the last run to insure a 10% replicate rate.

	Sn (1)	Fe (2)	Fe (3)	Ca (3)	Ca (4)	Si (5)
KOCHY-3	15002	46644	104330	31187	40273	22236
89-1296	-19	135	622	4550	5198	2976
89-1290	62	31552	227265	161503	167806	8041
89-1291	173	60318	87264	142630	146964	2712
89-1292	16	24477	11173	95930	100628	8826
89-1293	-14	77067	46163	50795	57736	1690
89-1294	115	84692	86391	61792	69555	1962
89-1295	32	50143	80394	119996	127154	9277
89-1308	51	76214	76214	40428	46120	8633
89-1309	79	22877	12283	81966	91009	4347
89-1310	118	26558	57078	76352	85132	1632

Input full *.RAW data file name (<CR> to end):

Figure 6-1. Computer display during SHOWQA Program.

Replicate data is examined during the data validation and spectra review step (Section 6.5). In general, the replicate $\mu g/cm^2$ data should be within ± 10% or within 3 times the reported analytical uncertainties. Exceptions to these criteria may be made for such species as chlorine and bromine, which may vaporize under the high vacuum and decrease between the first and second analyses.

6.3 Control Charts and Procedures

XRF performance charts are generated at the beginning of each month for the analyses run during the previous month. These charts present in graphical form the QA standard gross counts examined by XRFQA (Section 6.1).

When all of the runs for the previous month have been processed using PRXRF, change to the \XRF subdirectory on the c: drive of the Compaq 386 by typing **C: <Return>** and **CD\XRF <Return>**. Because the plotting program assumes the graphics screen printer driver is already available, the VGA resolution memory resident printing program must be loaded before starting the program: type **PRVGA <Return>**.

Start the QA plotting program by type **XRFQA <Return>**. The program will ask for confirmation that the printer driver is loaded (press **<Y>**, no <Return>). The program will ask for the number of the month for which plots are desired; enter a number 1 through 12 followed by a **<Return>**. A menu will appear specifying options for elements and conditions to be plotted (Figure 6-2). Under normal circumstances option 8 (autoprocessing) will be selected. Before selecting this option, make sure the dot matrix printer to the left of the Compaq 386 computer has at least 15 pages of paper, that the printer control switch is in the "Dot Matrix" position, and that the printer is on-line.

Press **<8>** (no <Return>) to select option 8. The program will automatically plot the data for each element and condition (6 plots in all), print the plot, and print a page of statistics (Figures 6-3 and 6-4). When the printing is completed, the program will again ask for the number of the month to be plotted. Press **<Return>** in response to this question to end the program. Type **COLOR <Return>** to turn off the Hercules emulation and return the display to VGA color resolution.

The plots are photocopied and the copies posted in the XRF room. The original printouts are delivered to the XRF Supervisor for review. Because the QA data is reviewed immediately after each run is processed with PRXRF, the plots will present any surprises, and no corrective action at this point is necessary.

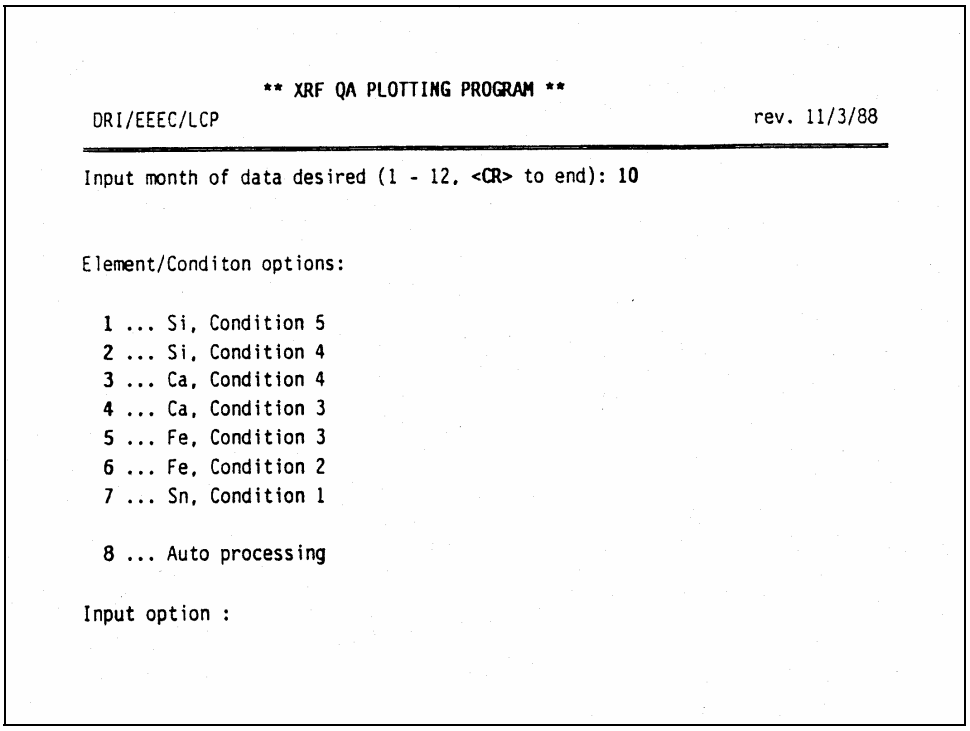


Figure 6-2. Computer Display during XRFQA Program.

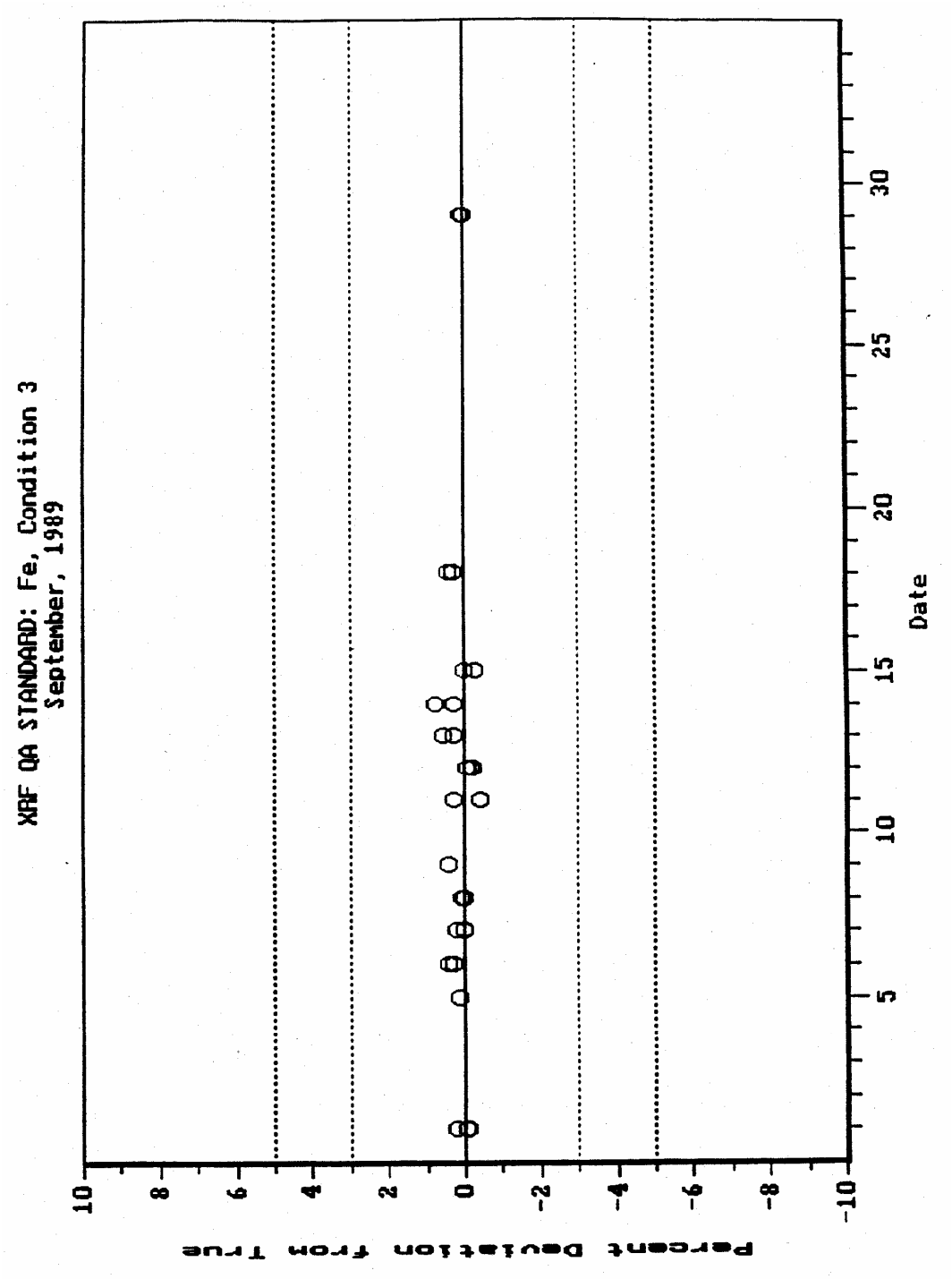
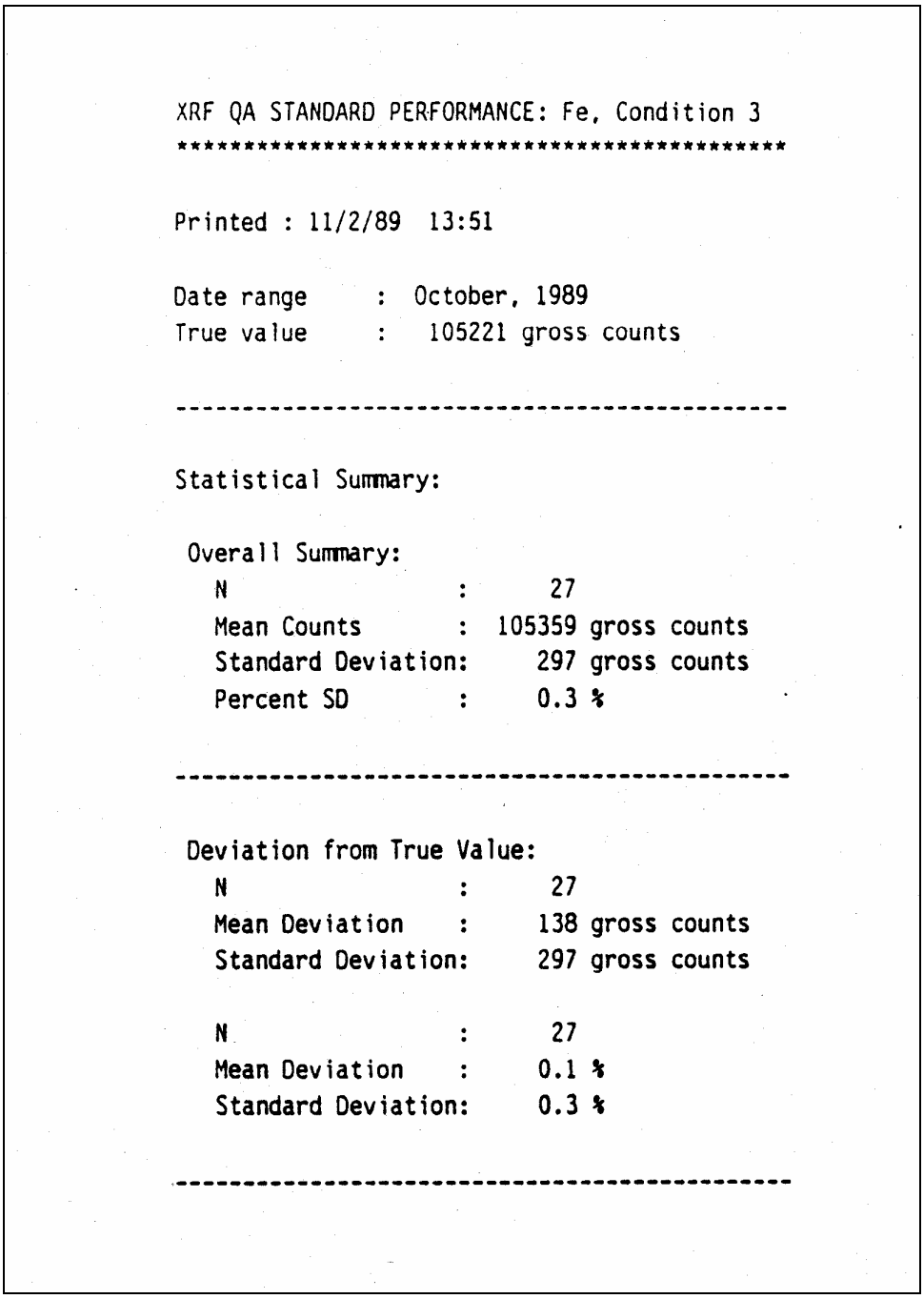


Figure 6-3. Example of XRF QA Plot.



```
XRF QA STANDARD PERFORMANCE: Fe, Condition 3
*******************************************

Printed : 11/2/89  13:51

Date range     :  October, 1989
True value     :   105221 gross counts

-------------------------------------------

Statistical Summary:

 Overall Summary:
   N                 :      27
   Mean Counts       :  105359 gross counts
   Standard Deviation:     297 gross counts
   Percent SD        :     0.3 %

-------------------------------------------

 Deviation from True Value:
   N                 :      27
   Mean Deviation    :     138 gross counts
   Standard Deviation:     297 gross counts

   N                 :      27
   Mean Deviation    :     0.1 %
   Standard Deviation:     0.3 %

-------------------------------------------
```

Figure 6-4. Example of XRF QA Statistical Analysis Printout.

Currently the replicate data is not plotted.

6.4 Validation Codes

XRF data and spectra validation codes are summarized in Table 6-1.

6.5 Data Validation and Feedback

The XRF Analysis Logsheet and attached printouts are reviewed by the XRF Supervisor or his designee. Any samples with incorrect or questionable data are noted on the XRF Validation Summary (Figure 6-5), along with steps taken to resolve any problems. Once all data has been validated and any necessary corrections made, the line labeled "QA Chks" on the XRF Analysis Logsheet is initialed and dated.

Begin data validation by verifying that all data entry is correct: sample ID's, deposit areas, and flags on the Logsheet and the printouts should match. If there are any discrepancies, note them on the XRF Validation Summary. For example, if the flag a sample is "i4" on the Logsheet, but appears as "i" on the printouts, record the XRF Run ID and the Filter ID on the XRF Validation Summary, and write "flag entered incorrectly" in the "Problem" column and "change flag to i4" in the "Action Taken" column.

Next, examine the printouts for internal consistency and "reasonableness" of the XRF data. Categories to check are inter-excitation condition agreement, presence of elements whose concentrations are usually below the detection limit, unusual elemental ratios, and replicate analysis results. Since data from the QA standard has already been checked, and since its composition is unlike aerosol samples, do not apply these checks to the QA standard. For the remaining samples, apply these validation steps one sample at a time as described below.

- The Tabular Data Printout (Figure 5-7) has a "Species Flag" column, which may contain one of three flags:

    l Concentration lower than minimum detectable limit.
    m Value from alternate excitation condition does not match value from normal excitation condition.
    u Value suspect - usually below detection limit for this element.

Table 6-1
XRF Validation Code Descriptions

Valid Code	Spcs Flag	Meaning		Resolution/Justification
1.	m	A1 cond 4 does not match cond 5 (Al intcnd agr poor).	1.1	Reanalyze.
			1.2	Agreement poor due to non-uniform deposit (Non-uniform).
			1.3	Cond 4 Al too low due to blank Al artifact peak (Cond 4 blank Al).
			1.4	Agreement poor due to poor cond 4 blank subtract (poor cond 4 bkgd).
			1.5	Cond 4 Higher due to lower incident x-ray absorption. Use cond 5 which is properly adjusted by particle size correction (Cond 4 lower abs).
			1.6	Cond 4 too high due to enhancement from large S, Cl, K, or Ca peak, >= 1/3 Ti sec. peak (S, Cl, K, or Ca enhancement).
2.	m	Si cond 4 does not match cond 5 (Si intcnd agr poor).	2.1	Reanalyze.
			2.2	Agreement poor due to non-uniform deposit (Non-uniform).
			2.3	Cond 4 Si too high due to tailing from S or Pb line (Cond 4 S or Pb tail).
			2.4	Cond 4 Si too high due to poor blank subtract at low (< 0.5 μg/cm2) conc. (Poor cond 4 bkgd).
			2.5	Cond 4 higher due to lower incident x-ray absorption. Use cond 5, which is properly adjusted by particle size correction (Cond 4 lower abs).
			2.6	Agreement poor due to metallic particles on filter (Metal particles).
			2.7	Cond 4 too high due to enhancement from large S, Cl, K, or Ca peak, >= 1/3 Ti sec. peak (S, Cl, K, or Ca enhancement).

Table 6-1 (continued)

Valid Code	Specs Flag	Meaning	Resolution/Justification	
3.	m	P cond 4 does not match cond 5 (P intcnd agr poor).	3.1	Reanalyze.
			3.2	Agreement poor due to non-uniform deposit (Non-uniform).
			3.3	Cond 4 P too high due to raised background from high Si (High Si).
			3.4	Cond 4 P too high due to tailing from S or Pb (Cond 4 S or Pb tail).
			3.5	Cond 4 P inaccurate due to poor background subtract (Poor Cond 4 bkgd).
			3.6	Cond 4 too high due to enhancement from large K peak, >= 1/3 Ti sec. peak (K enhancement).
4.	m	S cond 4 does not match cond 5 (S intcnd agr poor).	4.1	Reanalyze.
			4.2	Agreement poor due to non-uniform deposit (Non-uniform).
			4.3	Cond 4 S too high due to raised background from high Si (> 5 ug/cm2) (High Si).
			4.4	Cond 4 S not accurate due to poor background (Poor cond 4 bkgd).
5.	m	K cond 3 does not match cond 4 (K intcnd agr poor).	5.1	Reanalyze.
			5.2	Agreement poor due to non-uniform deposit (Non-uniform).
			5.3	Spectra OK. Agreement with 20% or 3 X unc. limits bat adequate for analysis needs (Agr accpt).
6.	m	Ca cond 3 does not match cond 4 (Ca intcnd agr poor).	6.1	Reanalyze.
			6.2	Agreement poor due to non-uniform deposit (Non-uniform).
			6.3	Cond 2 Ca inaccurate due to poor background subtract (Poor Cond 2 bkgd).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning	Resolution/Justification	
7.	m	Fe cond 2 does not match cond 3 (Fe intcnd agr poor).	7.1	Reanalyze.
			7.2	Agreement poor due to non-uniform deposit (Non-uniform).
			7.3	Spectra OK. Agreement not within 20% or 3 X unc. limits but adequate for analysis needs. (Agr accpt).
			7.4	Cond 2 Fe inaccurate due to poor background subtract (Poor cond 2 bkgd).
			7.5	Cond 2 Fe too high because Mn K beta interference not corrected (Uncorr Cond 2 Mn int).
			7.6	Agreement poor due to metallic particles on filter (Metal particles).
8.	m	Co cond 2 does not match cond 3 (Co intcnd agr poor).	8.1	Reanalyze.
9.	m	Ni cond 2 does not match cond 3 (Ni intcnd agr poor).	9.1	Reanalyze.
			9.2	Agreement poor due to non-uniform deposit (Non-uniform).
			9.3	Cond 2 Ni inaccurate due to poor background subtract (Poor Cond 2 bkgd).
			9.4	Agreement poor due to metallic particles on filter (Metal particles).
			9.5	Spectra OK. Agreement not within 20$ or 3 X unc. limits but adequate for analysis needs. (Agr accpt).
10.	m	Cu cond 2 does not match cond 3 (Cu intcnd agr poor).	10.1	Reanalyze.
			10.2	Agreement poor due to non-uniform deposit (Non-uniform).
			10.3	Cond 2 inaccurate due to interference from Ta L line (Cond 2 Ta int).
			10.4	Agreement poor due to metallic particles on filter (Metal particles).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning	Resolution/Justification	
11.	m	Zn cond 2 does not match cond 3 (Zn intcnd agr poor).	11.1	Reanalyze.
			11.2	Agreement poor due to non-uniform deposit (Non-uniform).
			11.3	Cond 2 inaccurate due to interference from Ta L line (Cond 2 Ta int).
			11.4	Agreement poor due to metallic particles on filter (Metal particles).
12.	u	Co cond 3 above detection limit (Co > DL).	12.1	Reanalyze.
			12.2	No Co peak present. Value too high due to improperly corrected Fe K beta. Change conc. to 0 +- 3 X unc. (No Co - Fe).
			12.3	Cannot tell if Co present at listed conc. due to Fe K beta interference. Data not changed. (Unresolved Co, Fe).
			12.4	Co peak present at about the listed conc. (Co peak vis).
			12.5	No Co peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Co - bkgd).
			12.6	Presence of Co not unusual in this set of samples. (Co common in set).
13.	u	Ga above detection limit. (Ga > DL).	13.1	Reanalyze.
			13.2	No Ga peak present. Value too high due to Ta L interference. Change conc. to 0 +- 3 X unc. (No Ga - Ta int).
			13.3	Cannot tell if Ga present at listed conc. due to Ta L interference. Data not changed. (Unresolved Ga, Ta).
			13.4	Ga peak present at about the listed conc. (Ga peak vis).
			13.5	Presence of Ga not unusual in this set of samples. (Ga common in set).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning	Resolution/Justification	
14.	u	As above detection limit. (As > DL).	14.1	Reanalyze.
			14.2	No As peak present. Value too high due to poor Pb L alpha or background correction. Change conc. to 0 +- 3 X unc. (No As - bkgd).
			14.3	Cannot tell if As present due to Pb L alpha interference - data not changed. (Unresolved As, Pb).
			14.4	As peak present at about the listed conc. (As peak vis).
			14.5	Presence of As not unusual in this set of samples. (As common in set).
15.	u	Se above detection limit. (Se > DL).	15.1	Reanalyze.
			15.2	No Se peak present. Value too high due to Pb L gamma interference. Change conc. to 0 +- 3 X unc. (No Se - Pb int).
			15.3	Se value too high due to filling in of background between Br and Pb. Change conc.to 0 +- 3 X unc. (No Se - bkgd).
			15.4	Se peak present at about the listed conc. (Se peak vis).
			15.5	Presence of Se not unusual in this set of samples. (Se common in set).
16.	u	Rb above detection limit. (Rb > DL).	16.1	Reanalyze.
			16.2	No Rb peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Rb - bkgd).
			16.3	Rb peak present at about the listed conc. (Rb peak vis).
			16.4	Presence of Rb not unusual in this set of samples. (Rb common in set).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning	Resolution/Justification
17.	u	Y above detection limit. (Y > DL).	17.1 Reanalyze. 17.2 No Y peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Y - bkgd). 17.3 Y peak present at about the listed conc. (Y peak vis). 17.4 Cannot tell if Y present due to Pb, Rb lines - data not changed. (Unresolved Y, Pb, Rb). 17.5 Presence of Y not unusual in this set of samples (Y common in set).
18.	u	Zr above detection limit. (Zr > DL).	18.1 Reanalyze. 18.2 No Zr peak present. Value too high due to poor background subtract on steep slope of scatter peak. Change conc. to 0 +- 3 X unc. (No Zr - bkgd). 18.3 Zr peak present at about the listed conc. (Zr peak vis). 18.4 Presence of Zr not unusual in this set of samples. (Zr common in set).
19.	u	Mo above detection limit. (Mo > DL).	19.1 Reanalyze. 19.2 No Mo peak present. Value too high due to poor background subtract on steep slope of scatter peak. Change conc. to 0 +- 3 X unc. (No Mo - bkgd). 19.3 Mo peak present at about the listed conc. (Mo peak vis). 19.4 Presence of Mo not unusual in this set of samples. (Mo common in set).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning	Resolution/Justification	
20.	u	Pd above detection limit. (Pd > DL).	20.1	Reanalyze.
			20.2	No Pd peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Pd - bkgd).
			20.3	Pd peak present at about the listed conc. (Pd peak vis).
21.	u	Ag above detection limit. (Ag > DL).	21.1	Reanalyze.
			21.2	No Ag peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Ag - bkgd).
			21.3	Ag peak present at about the listed conc. (Ag peak vis).
22.	u	Cd above detection limit. (Cd > DL).	22.1	Reanalyze.
			22.2	No Cd peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Cd - bkgd).
			22.3	Cd peak present at about the listed conc. (Cd peak vis).
			22.4	Presence of Cd not unusual in this set of samples. (Cd common in set).
23.	u	In above detection limit. (In > DL).	23.1	Reanalyze.
			23.2	No In peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No In - bkgd).
			23.3	In peak present at about the listed conc. (In peak vis).
24.	u	Sn above detection limit. (Sn > DL).	24.1	Reanalyze.
			24.2	No Sn peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Sn - bkgd).
			24.3	Sn peak present at about the listed conc. (Sn peak vis).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning		Resolution/Justification
25.	u	Sb above detection limit. (Sb > DL).	25.1	Reanalyze.
			25.2	No Sb peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Sb - bkgd).
			25.3	Sb peak present at about the listed conc. (Sb peak vis).
26.	u	Ba above detection limit. (Ba > DL).	26.1	Reanalyze.
			26.2	No Ba peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Ba - bkgd).
			26.3	Ba peak present at about the listed conc. (Ba peak vis).
			26.4	Presence of Ba not unusual in this set of samples (Ba common in set).
27.	u	La above detection limit. (La > DL).	27.1	Reanalyze.
			27.2	No La peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No La - bkgd).
			27.3	La peak present at about the listed conc. (La peak vis).
28.	u	Hg above detection limit. (Hg > DL).	28.1	Reanalyze.
			28.2	No Hg peak present. Value too high due to poor background subtract. Change conc. to 0 +- 3 X unc. (No Hg - bkgd).
			28.3	Hg peak present at about the listed conc. (Hg peak vis).
			28.4	No Hg present. Value too high due to uncorrected Ge interference (No Hg - Ge int).
			28.5	No Hg present. Value too high due to Fe + Ca sum peak (No Hg - Fe, Ca sum).
29.	--	Unusual ambient sample chemistry (Un amb chem).	30.1	Reanalyze.
			30.2	Spectra indicate run is good, no change indicated (Spectra OK).

Table 6-1 (continued)

Valid Code	Spcs Flag	Meaning	Resolution/Justification
30.	--	Unusual source sample chemistry (Un src chem).	31.1 Reanalyze. 31.2 Spectra indicate run is good, no change indicated (No change).
31.	--	Replicate does not match for element El (El rep bad).	32.1 Reanalyze run containing poor replicate (Reanalyze run). 32.2 Poor replicate due to non-uniform deposit (Non-uniform). 32.3 Reanalyze replicate only. Differences indicate sample specific, rather than run specific problem (Reanalyze rep). 32.4 Spectra virtually identical except for lower Cl peak in replicate, indicating loss of volatile Cl. (Loss vol Cl).

Notes: 1. Criteria for matching of inter-excitation condition values is <= 20% ave. difference, or difference <= 3*(sum of unc.).
2. Criteria for matching of replicate values is <= 10% ave. difference, or difference <= 3*(sum of unc.).

XRF VALIDATION SUMMARY

Project Santa Barbara Initial CAF Date 891108

XRF Run	Filter ID	Cond	Problem	Results of Spectra Check	Action Taken	✓
SABA-17	AT6028	5	Al << 0	Bkgd too high	Δ Al to 0.1507 μgkm²	✓
	AT6032	2	Se > DL	VC 15.4		
SABA-18	AT6034	2	Se > DL	VC 15.4		
	BT1046	2	Se > DL	VC 15.4		
	BT1052	1	Ag > DL	no Ag - Bkgd	Δ to 0 if 3*σ	✓
	AT6030-R		hi flag missing		Δ flag to r1 b1	✓
SABA-19	AT2045	2	Se > DL	VC 15.4		
	GT2051	2	Ba > DL	Ba pk vis		
	MT4044	2	Se > DL	VC 15.4		
SABA-20	WT3034	2	Se > DL	VC 15.4		
SABA-21	WT3036	5	Al << 0	Bkgd too high, no Al pk		
		3,2	Fe intcnd agr poor	Cond 2 ok		
		2	Se > DL	VC 15.4		
	YT5043	2	Se > DL	VC 15.4		
	YT5051	2	Se > DL	VC 15.4		

1/7/89-88

Figure 6-5. Example of Completed XRF Validation Summary Sheet.

- For elements measured by two excitation conditions, the difference in concentrations must be <= 20% of the average concentration, or <= 3 times the sum of the uncertainties. If these criteria are not met, the "m" species flag is applied by program PRXRF. For each element that is flagged "m", refer to Table 6-1, DRI XRF Validation Flags, for possible explanations for the "m" flag. If one of the listed explanations applies, write its validation code on the printout next to the "m" flag to indicate that the discrepancy has been resolved. For example, if a sample has an "m" flag for Si, with Condition 4 higher than Condition 5, and S concentration is 5 times Si, validation code 2.3 applies (Cond. 4 Si too high due to tailing from S line). Write 2.3 on the printout next to the "m" flag. If none of the listed explanations apply, put a check mark beside the "m" flag on the printout and fill in the "XRF Run", "Filter ID", "Cond" and "Problem" columns of the XRF Validation Summary. Use the abbreviations listed in Table 6-1 to save time.

- Elements that are usually below detection limits, Co, Ga, As, Se, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl and U, are flagged "u" if their concentrations are greater than the uncertainty. For each element that is flagged "u", refer to Table 6-1 for possible explanations for the "u" flag. If one of the listed explanations applies, write its validation code on the printout next to the "u" flag. If none of the listed explanations apply, put a check mark beside the "u" flag on the printout and fill in the appropriate columns on the XRF Validation Summary.

- After checking for "m" and "u" flags, evaluate the data with respect to concentration ratios. Concentration ratios vary dramatically among different sample types, but after reviewing data from many samples of a particular location or source, samples with unusual elemental concentration ratios will be easy to identify. As an example, suppose you are reviewing analysis results of ambient PM_{10} samples where the Al/Si ratio is typically 0.25 to 0.4. If one sample has an Al/Si ratio of 0.8, it should be noted. Identify unusual elemental ratios by noting the unusual ratio on the printout and recording the appropriate information on the XRF Validation Summary. See Table 6-1 for the validation codes and abbreviations to use.

- Check agreement between replicate analysis results and the original. Replicate samples are indicated with an "r1" sample flag, and with "-R" appended to the sample ID. The difference between replicate and original analysis concentrations should be <= 10% of the average concentration, or <= 3 times the sum of the uncertainties. If the replicate meets these criteria, write "Rep OK" on the printout. If the criteria are not met, and if one of the explanations given for poor replicates in Table 6-1 does not apply, write "Poor replicate for element:", and the element mnemonic, on the printout and the XRF Validation Summary.

After completing the validation steps for each sample in a run, resolve problems recorded on the XRF Validation Summary in the following manner. For runs that have a poor replicate, reanalyze the entire run. Resolve other problems by looking at spectra or at the actual sample itself.

Inter-excitation condition results that do not match ("m" flag) can often be traced to a non-uniform deposit. Examine samples visually and under a microscope to see if a non-uniform deposit is present. Look in particular for large particles that are not uniformly distributed, or for metallic particles, as these conditions will often result in "m" flags. Closed-face

aerosol sample holders and open-faced sample holders that do not allow sufficient flow collimation can result in "impaction" of coarse particles in the center of the deposit. If the deposit is non-uniform or contains metallic particles, note in the "Results of Spectra Check" column of the XRF Validation Summary, and write "change flag to", followed by the appropriate flag in the "Action Taken" column.

Examine spectra of remaining samples with "m" or "u" flags to see if there are any obvious irregularities. The Operating System Description part of Section 2.1.1 describes how to display selected spectra. Use REC/COMP to superimpose background spectra on a sample spectrum.

For samples with "u" flags, check particularly to see if a peak is present. It may be necessary to check the background subtraction for concentrations near the detection limit. Bear in mind the potential peak overlaps. Use the KLM markers or the Kevex x-ray energy slide rule to find overlaps. If no peak exists for an element flagged "u", write the reason (such as background or interference from another peak) in the "Results of Spectra " column and "change to 0 +- 3 * σ" in the "Action Taken" column of the Validation Summary. Refer to Table 6-1 for abbreviations to use. If there is a peak, note in the "Result" column.

If any problem listed on the Validation Summary cannot be resolved, the sample must be reanalyzed. Indicate this in the "Action Taken" column. After all problems have been resolved, or reanalysis indicated, the data must be read into a dBase file. Do this by changing to the project subdirectory in DOS, and typing **DBASE <Return>**. Then type **DO XRFINP <Return>** and enter the file name given on the sample analysis list. Using the dBase BROWSE command, change values, flags, sample ID's as listed on the XRF Validation Summary and record changes made in the "XNOTE" field.

Delete records for samples to be reanalyzed by pressing **<Ctrl U>**. After making all changes, save changes to the file by pressing **<Ctrl END>**. If any records were deleted, give the command **PACK <Return>**. Verify changes by BROWSEing the file again and making sure changes were made correctly.

When all data has been entered into a dBase file and all necessary corrections made, indicate so by initialing and dating the "QA Chks" line of the XRF Analysis Log. Punch the XRF Validation Summary along with the XRF Analysis Log and printouts and bind in a folder labeled with project, XRF run numbers and date.

7.0 REFERENCES

Kevex Corporation, "Radiation Safety Guide for Users of Kevex Equipment", Foster City, CA, rev. April, 1985.

University of Nevada System, "Radiation Safety Manual", Reno, NV, rev. Oct., 1982.

Kevex Corporation, "Kevex 0700 User's Manual", Foster City, CA, rev. June, 1984.

Kevex Corporation, "Kevex Analyst 8000 User's Manual, Foster City, CA, rev. August, 1986.

Kevex Corporation, "Kevex XRF Toolbox Tutorial", Foster City, CA, August, 1986.

Kevex Corporation, "Kevex XRF Toolbox Reference Manual", Foster City, CA, rev. August, 1986.

APPENDIX A.5

DRI STANDARD OPERATING PROCEDURE Pages: 63
Title: Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples Number: 2-204.6 Revision: 6

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This standard operating procedure is intended to:

- provide a basic understanding of the principles of carbon analysis and carbon analyzer operation;
- describe routine determination of organic, elemental, and carbonate carbon from ambient and source filter samples using the DRI thermal/optical reflectance carbon analyzer;
- detail the concerns and procedures that will insure a state-of-the-art carbon analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility of the Division of Atmospheric Sciences at the Desert Research Institute.

1.2 Measurement Principle

The DRI thermal/optical carbon analyzer is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (normally 0.536 cm^2) taken from a quartz fiber filter; 2) converting these compounds to carbon dioxide (CO_2) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO_2); 3) reduction of CO_2 to methane (CH_4) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH_4 equivalents by a flame ionization detector (FID).

The principal function of the optical (laser reflectance) component of the analyzer is correction for pyrolysis of organic carbon compounds to elemental carbon. Without this correction, the organic carbon fraction of the sample would be underestimated and the elemental carbon fraction would be overestimated by including some pyrolyzed organic carbon. The correction for pyrolysis is made by continuously monitoring the filter reflectance (via a helium-neon laser and a photodetector) throughout an analysis cycle. This reflectance, largely dominated by the presence of light absorbing elemental carbon, decreases as pyrolysis takes place and increases as light absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be accurately

assigned to the organic fraction. The correction for pyrolytic conversion of organic to elemental carbon is essential for an unbiased measurement of both carbon fractions, as discussed in Johnson et al. (1981).

Carbonate carbon can be determined by measuring the CO_2 evolved upon acidification of the sample punch before the normal carbon analysis procedure.

Seven temperature fractions as well as the pyrolysis correction are individually determined and can be reported. Values routinely reported include total organic carbon, organic carbon evolved at temperatures greater than 120°C (high-temperature organic carbon), total elemental carbon, elemental carbon evolved at temperatures greater than 550°C (high-temperature elemental carbon), total carbon, and carbonate.

1.3 Measurement Interferences and Their Minimization

- Carbonate carbon presents significant interference in carbon analysis if it constitutes more than 5% of total carbon in the ambient or source sample, as it is measured as both organic and elemental carbon during thermal/optical carbon analysis. Acid pretreatment of the filter samples can eliminate the carbonate interference.

- The presence of certain minerals in some soils can affect the laser correction for pyrolysis. These minerals change color as the sample punch is heated, generally resulting in a sample which is darker. For samples which contain large fractions of resuspended soils, the split between organic and elemental carbon should be examined manually.

- Some minerals, again predominantly in soil samples or soil dominated samples, may affect the laser reflectance by temporarily changing color or changing the surface texture of the deposit residue. Unlike the effect described above, these changes are reversible and highly temperature dependent.

- Some colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed. This effect is readily ascertained by examining the laser response during the organic portion of the analysis. The split between organic and elemental carbon should be examined manually if the effect is large.

- The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr), existing either as contaminants on the filters (e.g., glass fiber filters) or as part of the deposit material, has been shown to catalyze the removal of elemental carbon at lower temperatures (Lin and Friedlander, 1988). Such catalysis would affect the distribution of carbon peaks during the analysis.

- Water vapor, either contained in the deposit or remaining after acidification of the sample punch, can shift the FID baseline. Allowing the sample punch to dry in the analyzer by passing carrier gases over it will eliminate this effect.

1.4 Ranges and Typical Values of Measurements

A wide range of aerosol concentrations can be measured with this method, the limiting factor being the concentration of the carbon compounds on a μg/filter basis. Heavily polluted environments, which would normally have carbon concentrations above the working range of the carbon analyzer, may be sampled and analyzed within the range of the carbon analyzer by increasing the filter deposit area or by decreasing the sampling flow rate and/or sampling time.

The carbon analyzer can effectively measure between 0.05 and 750 μg carbon/cm^2. The upper range is somewhat arbitrary, depending on the particular compounds on the filter and the temperatures at which they evolve. This upper range may be extended by taking special precautions, such as reducing the punch size or by special temperature programming, to avoid an over-range FID signal.

Typical carbon values range between 10 and 100 μg carbon/cm^2 for ambient samples. The distribution between organic and elemental carbon depends on the particulate source types, and range from no elemental carbon (e.g., hot gasoline exhaust) to 80% or more elemental carbon (e.g., woodsmoke and diesel exhaust).

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The lower quantifiable limits (LQLs) of carbon combustion methods depend upon the variable carbon content of the blank quartz filters as well as the analysis method. For better LQLs, the unexposed filters should be pre-fired in an oven at high temperatures for several hours to remove any residual carbon contamination (Fung, 1986; Huntzicker, 1986; Rau, 1986). All quartz filters originating from DRI are pre-fired for a minimum of four hours at 900°C and are acceptance-tested for blank levels before use. Any filters that fail to pass the preset acceptance levels (1.5 μg/cm^2 organic carbon, 0.5 μg elemental carbon, and 2.0 μg total carbon) are discarded and not used for sample collection. Average pre-fired blank levels are 0.41 ± 0.2 μg organic carbon/cm^2, 0.03 ± 0.2 μg elemental carbon/cm^2, and 0.44 ± 0.2 μg total carbon/cm^2. Because even pre-fired filters can absorb organic vapors during shipping and storage, the LQL of analysis on a particular set filters depends on the number of field blanks analyzed and the variability in the results from those blanks.

The minimum detection limit (MDL) of the DRI carbon analyzers based on the analyses of 693 individual quartz-fiber filters and defined as three times the standard deviation of their measured results. They are:

total organic carbon	0.82 μg/cm^2
high-temperature organic carbon	0.81 μg/cm^2
total elemental carbon	0.19 μg/cm^2
high-temperature elemental carbon	0.12 μg/cm^2
total carbon	0.93 μg/cm^2

Acid-evolved carbonate levels in pre-fired quartz filters have been shown to be quite variable (0.0-1.0 μg/cm^2) over time. The reaction of ambient CO_2 with alkaline sites on the quartz fibers may be the cause of such variable blank levels. Acceptance testing for carbonate is not routinely performed at DRI, as carbonate analysis is performed only upon special request by the client.

The precision of this analysis has been reported to range from 2 to 4% (Johnson, 1981). For analysis of actual ambient and source filters, homogeneity of the deposit is most important for reproducible results. For homogeneous deposits containing >10 μg/filter of total carbon, precision is generally 5% or less; for inhomogeneous deposits replicates may deviate by as much as 30%. The precision of carbonate analysis results is approximately 10%.

The precision of the laser-dependent split between organic and elemental carbon fractions depends upon how rapidly the laser is increasing at the time of the split and whether the split falls in the middle of a large carbon peak or not. Typically, relative laser split times are reproducible within 10 seconds and deviations in calculated splits are less than 5% of the total measured carbon.

The accuracy of the thermal/optical reflectance method for total carbon determined by analyzing a known amount of carbon is between 2 to 6% (Rau, 1986). Accuracy of the organic/elemental carbon split is between 5 and 10%.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing carbon analysis, which includes routine system calibration, actual analysis, and immediate review of the data as it is produced to correct system problems.

It is the responsibility of the laboratory manager or supervisor to ensure the carbon analyses procedures are properly followed, to examine and document all replicate, standard, and blank performance test data, to designate samples for reanalysis, to arrange for maintenance and repair, to maintain the supplies and gases necessary to insure uninterrupted analysis, and to deliver the analysis results in database format to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Division of Atmospheric Sciences is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used in this document:

Calibration Injection: The injection of calibration gases (methane in helium [CH_4/He] or carbon dioxide in helium [CO_2/He]) into the sample stream to check instrument performance.

Calibration Peak: The FID peak resulting from the automatic injection of methane calibration gas (CH_4/He) at the end of each analysis run (each sample). All integrated peak areas are divided by the calibration peak area and multiplied by an instrument-specific calibration factor to obtain μg carbon.

FID Split Time: The time at which the laser split occurs plus the time required for carbon compounds to travel from the sample punch to the FID.

High Temperature Elemental Carbon: Carbon evolved from the filter punch in an oxygen/helium (O_2/He) atmosphere at 700 and 800°C minus any pyrolyzed organic carbon present in these two peaks.

High Temperature Organic Carbon: Carbon evolved from the filter punch in a He-only atmosphere at 250, 450, and 550°C plus pyrolyzed organic carbon. This is the same as regular OC without the first organic carbon peak (VOC).

Laser Split: The demarcation between organic and elemental carbon, at which the laser-measured reflectance of the filter punch reaches its initial value. At this point all pyrolyzed organic carbon has been removed and original elemental carbon is beginning to evolve.

Lower Split Time: The time at which the laser-measured reflectance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).

Pyrolysis: The conversion of organic carbon compounds to elemental carbon due to incomplete combustion/oxidation; may be envisioned as "charring" during the organic portion of the analysis.

Pyrolyzed Carbon: The carbon evolved from the time that the carrier gas flow is changed from He to He/O_2 at 550°C to the time that the laser-measured filter reflectance reaches its initial value.

Regular Elemental Carbon (EC): Carbon evolved from the filter punch in a helium/ oxygen (He/O_2) atmosphere at 550, 700, and 800°C minus pyrolyzed organic carbon.

Regular Organic Carbon (OC): Carbon evolved from the filter punch in a He atmosphere at 120, 250, 450, and 550°C plus pyrolyzed organic carbon. This is the same as VOC plus high temperature OC.

Regular Split Time: The time at which the laser-measured reflectance of the filter punch reaches its initial value.

Total Carbon (TC): All carbon evolved from the filter punch between ambient and 800°C under He and O_2/He atmospheres.

Upper Split Time: The time at which the laser-measured reflectance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).

Volatile Organic Carbon (VOC): Organic carbon evolved from the filter punch in a He-only atmosphere between ambient and 120°C (the first organic carbon peak).

1.8 Related Procedures

SOP's related to carbon analysis activities and other manuals which should be reviewed in conjunction with this document are:

DRI SOP #6-001.1 Shipping and Mailing Procedures.

DRI SOP #6-009.1 Field and Laboratory Safety Procedures.

DRI SOP #4-001.1 Creation, Revision, Distribution, and Archiving of Standard Operating Procedures.

DRI SOP #2-106.3 Pre-Firing of Quartz Filters for Carbon Analysis

The DRI Carbon Analyzer Model 3000 Owner's Manual, revised 6/90.

The DRI Carbon Analyzer Model 3000 Maintenance and Troubleshooting Manual, revised 7/94.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The components of the DRI thermal/optical carbon analyzer are depicted in Figures 2-1 and 2-2; the complete gas flow schematic is shown in Figure 2-3. The programmable combustion oven is the heart of the carbon analyzer and includes loading, combustion, and oxidation zones in a single quartz "oven" as depicted in Figure 2-4.

In addition to the DRI thermal/optical analyzer connected to a Pentium compatible computer, the following items are needed for routine carbon analysis:

- Stainless steel punching tool: 0.516 cm^2 area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp. If the punching tool is sharpened, the punch area must be reverified.

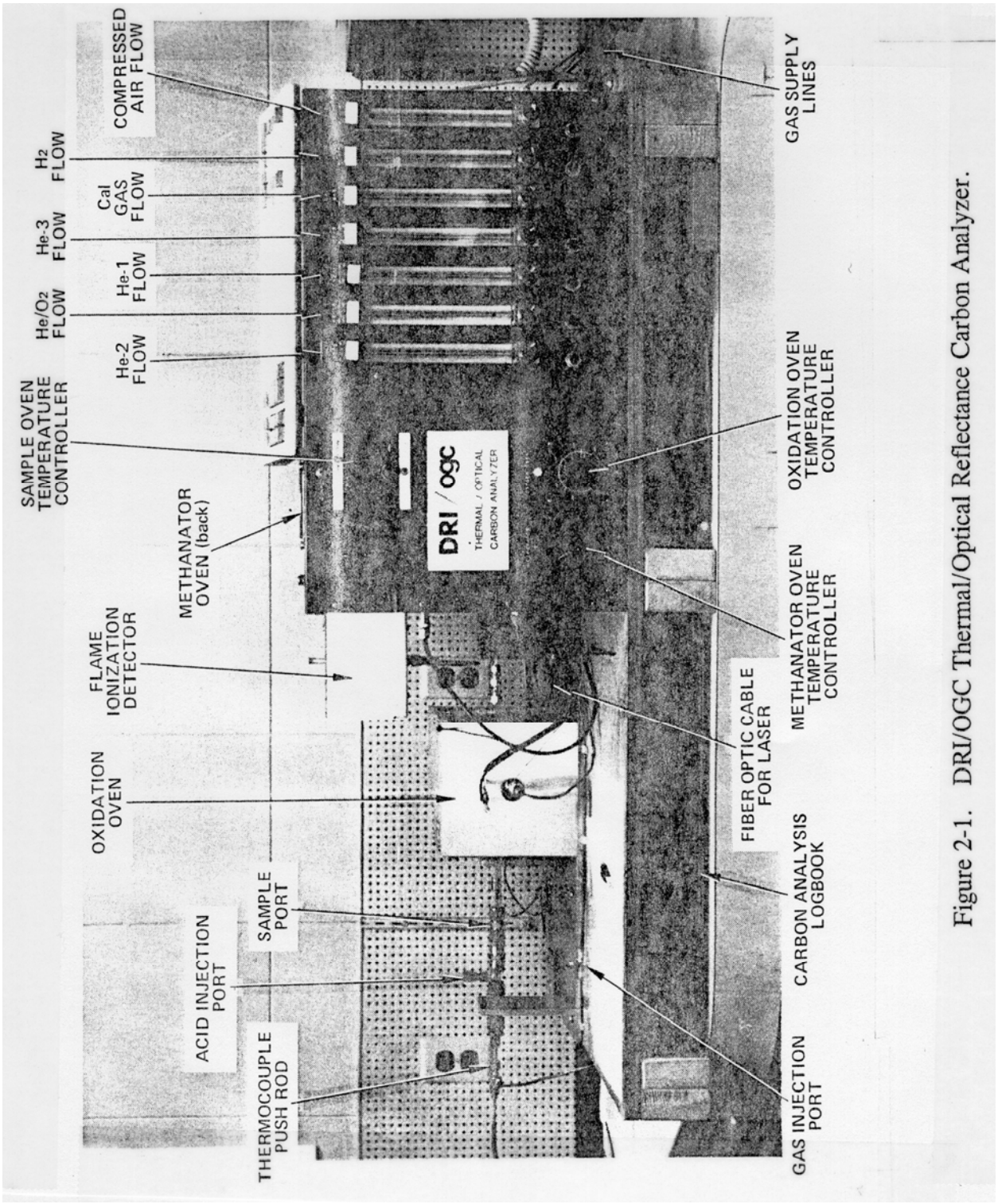


Figure 2-1. DRI/OGC Thermal/Optical Reflectance Carbon Analyzer.

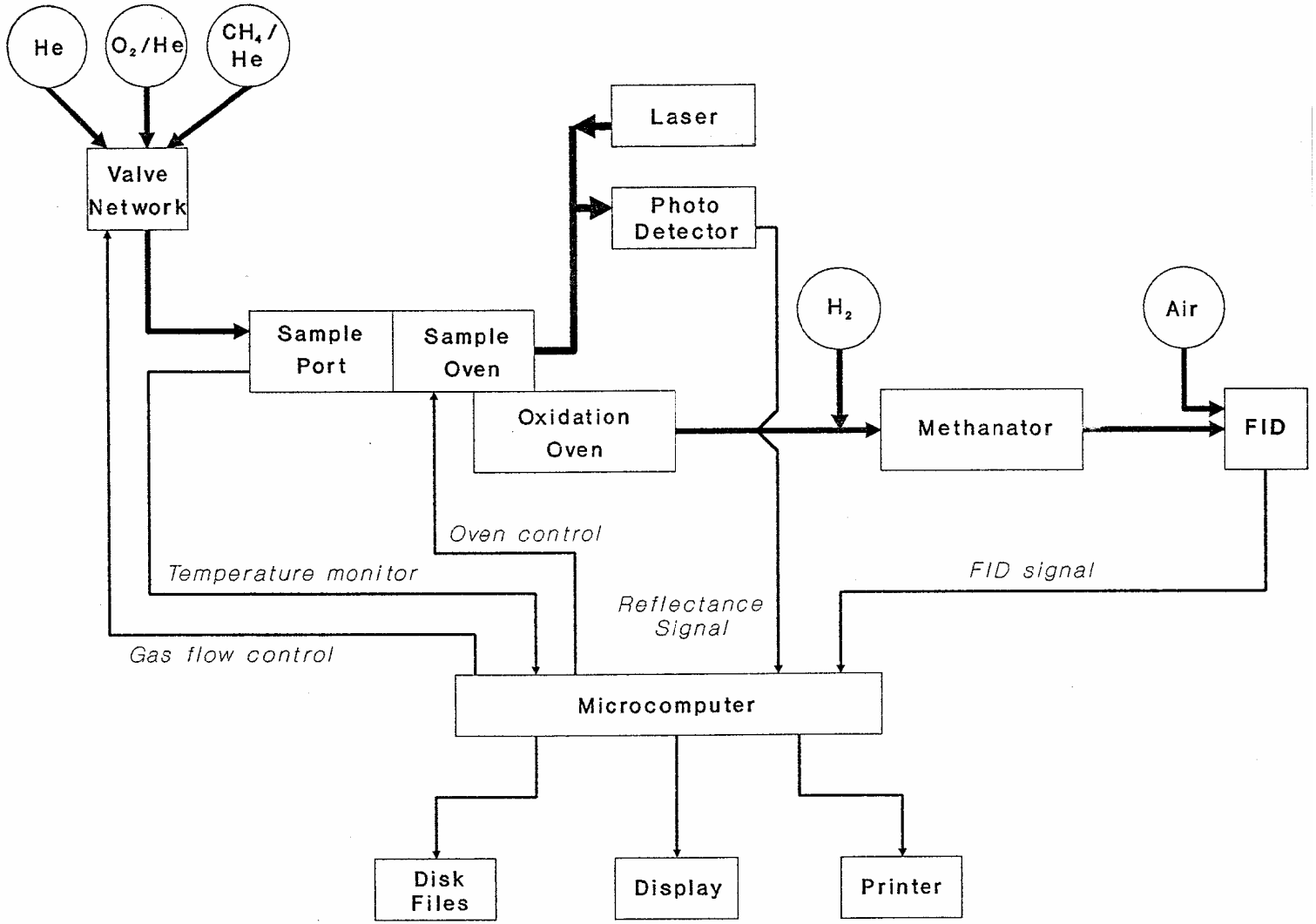


Figure 2-2. DRI/OGC Thermal/Optical Reflectance Carbon Analyzer Block Diagram.

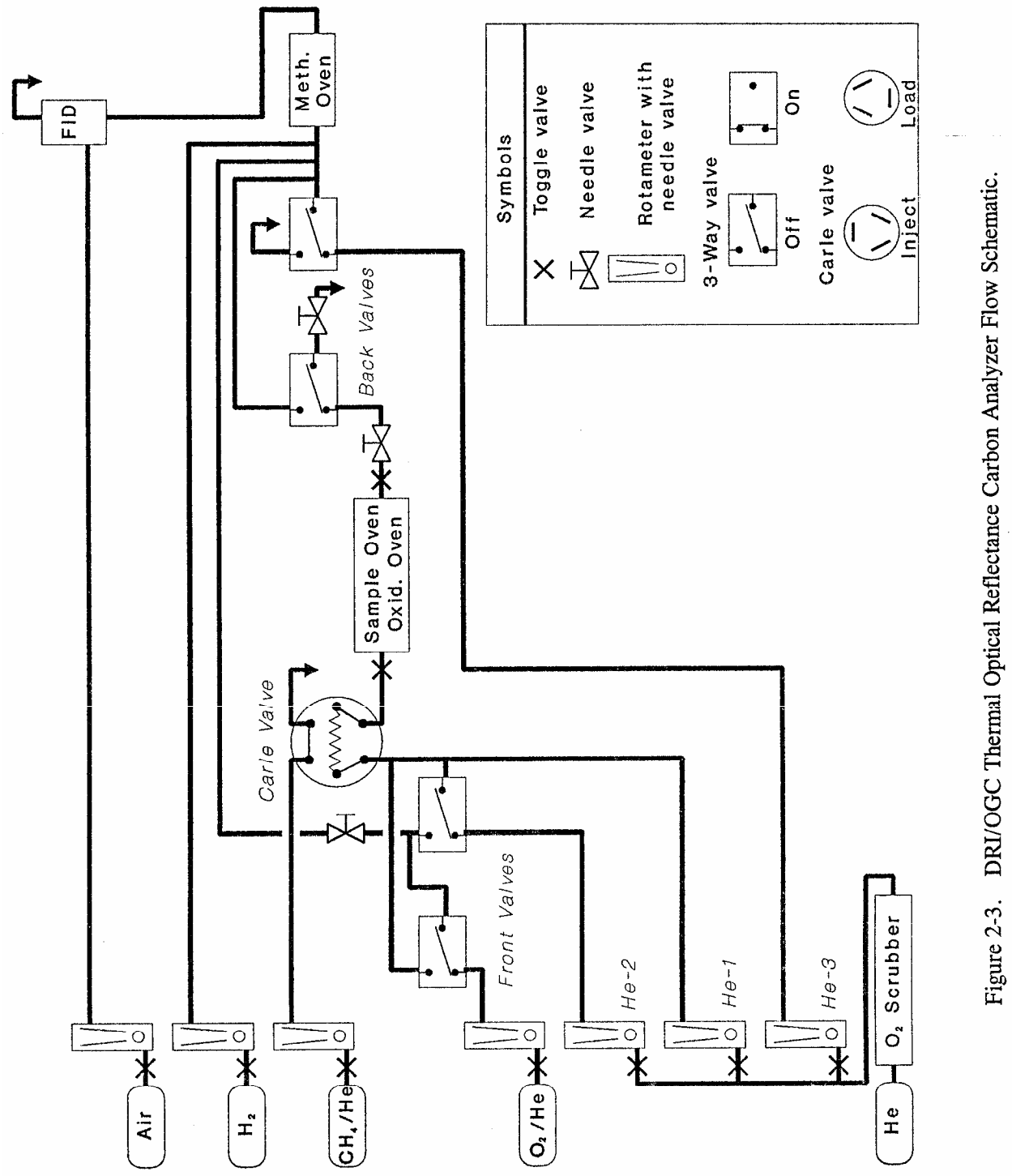


Figure 2-3. DRI/OGC Thermal Optical Reflectance Carbon Analyzer Flow Schematic.

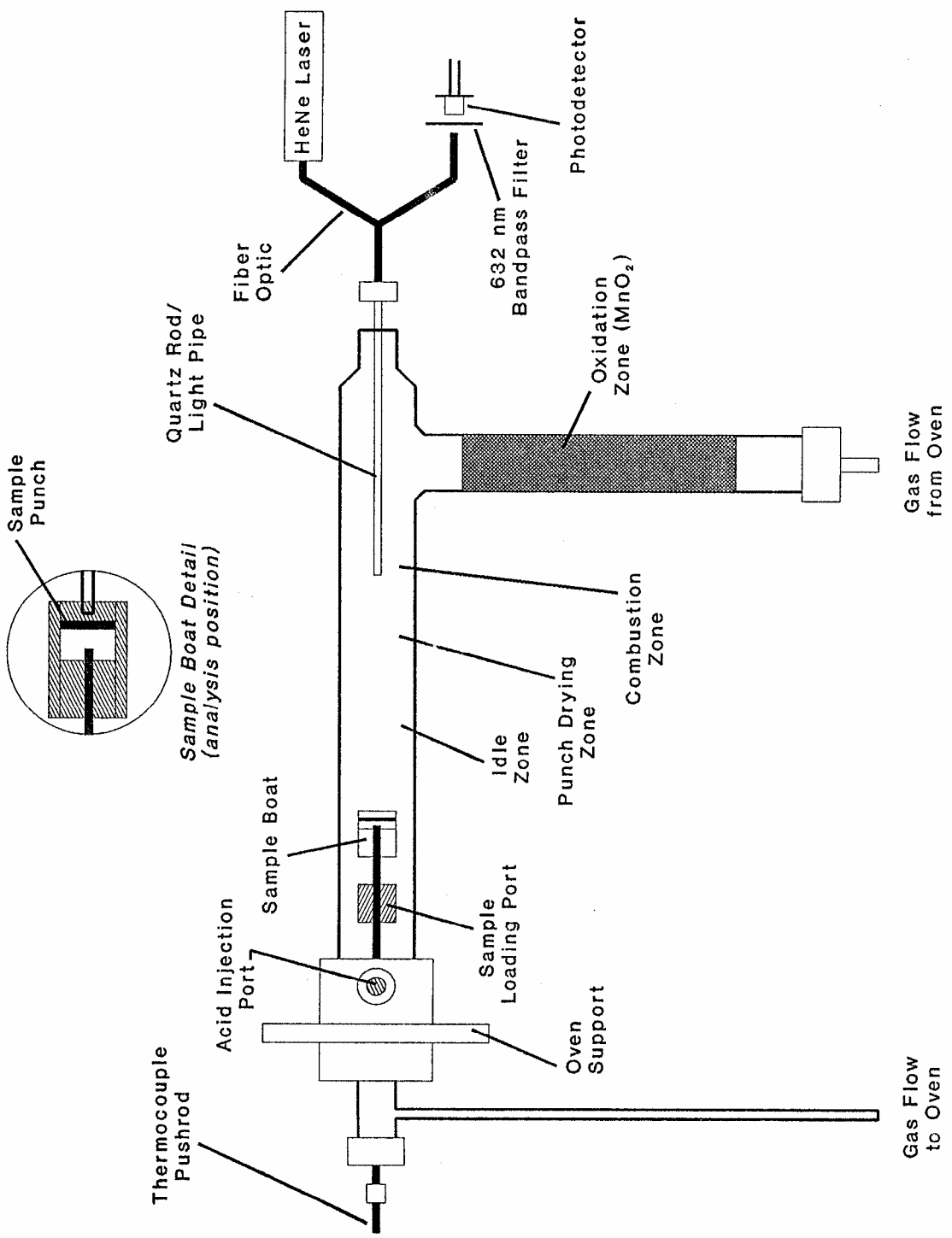


Figure 2-4. DRI/OGC Thermal/Optical Reflectance Carbon Analyzer Combustion Oven.

- Syringes: Hamilton gas-tight 1000 and 2500 ml syringes for calibration injections; 25 ml syringe for carbonate analysis and for analyzer calibration.
- Quartz filters: Pallflex 2500 QAT-UP or equivalent.
- Tweezers.
- Glass petri dish.
- Logbook/notebook.
- Transparent tape.
- Kimwipes.
- Small cooler.
- Blue ice.
- Butane lighter to light the FID.
- Small adjustable wrench.
- A copy of CARBON.EXE (the analysis program), version 4.0 or later, and CARBON.DAT (the analysis parameter file), version 4.0 or later.

2.1.2 Instrument Characterization

The DRI carbon analyzer is program-driven and data is stored automatically to disk via an Pentium compatible computer. Response times and signal lag times are built into the parameter file which is loaded when the analysis program begins. The program is event driven; that is, when the FID signal returns to its baseline after a minimum of 80 seconds at one analysis condition, the program will advance to the next temperature or carrier gas mixture. A maximum time limit per analysis condition is also established to prevent a slight baseline drift from holding the analyzer in one condition indefinitely. This method requires no sample pretreatment, requires between 15 and 70 minutes of analysis time per sample, requires at least one 0.516 cm^2 punch per filter, and destroys the sample punch.

Operator concerns for correct routine operation of the instrument include the following (refer to section 4 for more details):

- Insure that the sample port is tight after loading a sample punch.
- Remember to push the sample in when the computer tone sounds (Section 4.3); DO NOT leave the room until the analysis begins.
- Insure that the thermocouple is physically decoupled from the sample boat after pushing in the sample to prevent oven temperature from influencing the laser reflectance signal.

- Check the graphical printout after each analysis run to insure that the FID, temperature, and laser signals are behaving as expected (Section 4.3). Report any anomalies to the lab supervisor immediately.

- The quartz oven is susceptible to breakage, especially at the sample port. Care should be taken to avoid exerting tangential pressure on the oven when manipulating the sample port fitting.

2.1.3 Maintenance

Regular maintenance for the analyzer involves daily checking of compressed gas supplies, cleaning the punching tool and tweezers between each sample with dry KimWipes (Kimberly-Clark Corporation), and backing up data files on a daily basis. Checks of laser adjustments (physical and electrical) are made at least monthly; analyzer calibrations are performed every six months. All calibrations and repairs must be recorded in the log book. Additionally, all repairs must be recorded in the maintenance log book.

Refer to the maintenance and troubleshooting guide for additional information.

2.1.4 Spare Parts

The following spare parts must be kept on hand to insure minimal interruptions in carbon analysis:

- Quartz rods: 3 mm nominal diameter, Homosil optical quality rod, (GM Associates, Oakland), cut to 9-$^{3}/_{4}$" lengths and polished on both ends using a lap polisher.

- Quartz ovens: specially built ovens by Adams & Chittenden Scientific Glass, 1414 Fourth St., Berkley, CA 94710, voice: (510) 524-9551, fax: (510) 524-955, contact person: Tom Adams. Or by Glasstech, La Plata, MD, voice: (301) 392-0723, contact person: Mike Trembly.

- Quartz boats: made at DRI from scraps of broken ovens.

- Thermocouple rods: 12" length by 1/8" OD, type K ground isolated with 316 stainless steel sheaths (Omega, Part # TJ36-CAIN-18U-18).

- FID flame tips: for Gow-Mac #12-800 FIDs (Gow-Mac, #132-117). Gow-Mac Instrument Co., P.O. Box 25444, Lehigh Valley, PA 18002-5444, voice: (610) 954-9000, fax: (610) 954-0599.

- Septa: 1/4" and 1/8", for injection ports.

- Replacement needles for syringes.

- Replacement oxygen/moisture trap (R&D Separations, Model OT3-2).

- Replacement hydrocarbon trap (R&D Separations, Model HT200-4).

- Replacement indicating oxygen trap (Chromatography Research Supplies, Model 202223).
- Stainless steel wire: for forming "ears" to hold the sample boat in position and for wrapping the "ears" onto the thermocouple push rod (Rocky Mountain Orthodontics, #RMO E-19, 0.914 mm).
- Quartz wool: for repacking the oxidation oven (Alltech Associates, #4033).
- Teflon ferrules: Parker or Swagelok style, 1/2" ID, for the sample port fitting.
- Teflon ferrules: 1/2" OD by 1/8" ID, for the thermocouple rod at the back of the oven.
- Heating element for oven: custom made 650 W coiled heater (Marchi-Norman Associates #SDH175). Marchi-Norman Associates, Inc., 630 Price Ave., Redwood City, CA 94063, voice: (415) 364-3411, fax: (415) 364-4138.
- FID battery: 300 VDC (EverReady #495).
- Printer paper.
- Printer toner cartridge.
- Computer super disks, LS-120.

2.2 Reagents

The following chemicals should be reagent grade or better:

- Potassium hydrogen phthalate (KHP), for calibration use (Fisher, #P-243).
- Sucrose, for calibration use (EM Science, #SX1075-1).
- Manganese dioxide (MnO_2), crystalline, as an oxidizer in the oxygen oven (Nurnberg Scientific, #C5162).
- Nickelous Nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], crystalline, used as a reducer in the methanator (Fisher Scientific, cat # N62-500, CAS 13478-00-7).
- Chromosorb 60/80 mesh, used as a support for nickel catalyst in methanator (Supelco, catalog # 2-0165).
- Hydrochloric acid (HCl), 0.4 molar solution, for use in cleaning punch and quartz ovens, and for use in carbonate analysis.
- Distilled deionized water (DDW): total carbon background should be 6 ppm or less (determined as described in Section 5.1).

2.3 Gases

The following compressed gases should be industrial grade or better:

- Helium for a carrier gas, regulated to 15-20 psi with a metal diaphragm regulator. The higher pressure is required due to the pressure drop across the oxygen/moisture and hyrdrocarbon traps.

The laboratory supervisor will determine the minimum delivery pressure necessary for proper helium flows.

- 5% methane by volume in helium for calibration injections and calibration peaks; regulated to 10 psi by a metal diaphragm regulator, NIST traceable.

- 5% carbon dioxide by volume in helium for calibration injections; regulated to 10 psi by a metal diaphragm regulator, NIST traceable.

- 10% oxygen by volume in helium as a carrier gas, regulated to 10 psi by a metal diaphragm regulator.

In addition, the following gases are required:

- Hydrogen for the FID flame, regulated to 17 psi with a metal diaphragm regulator.

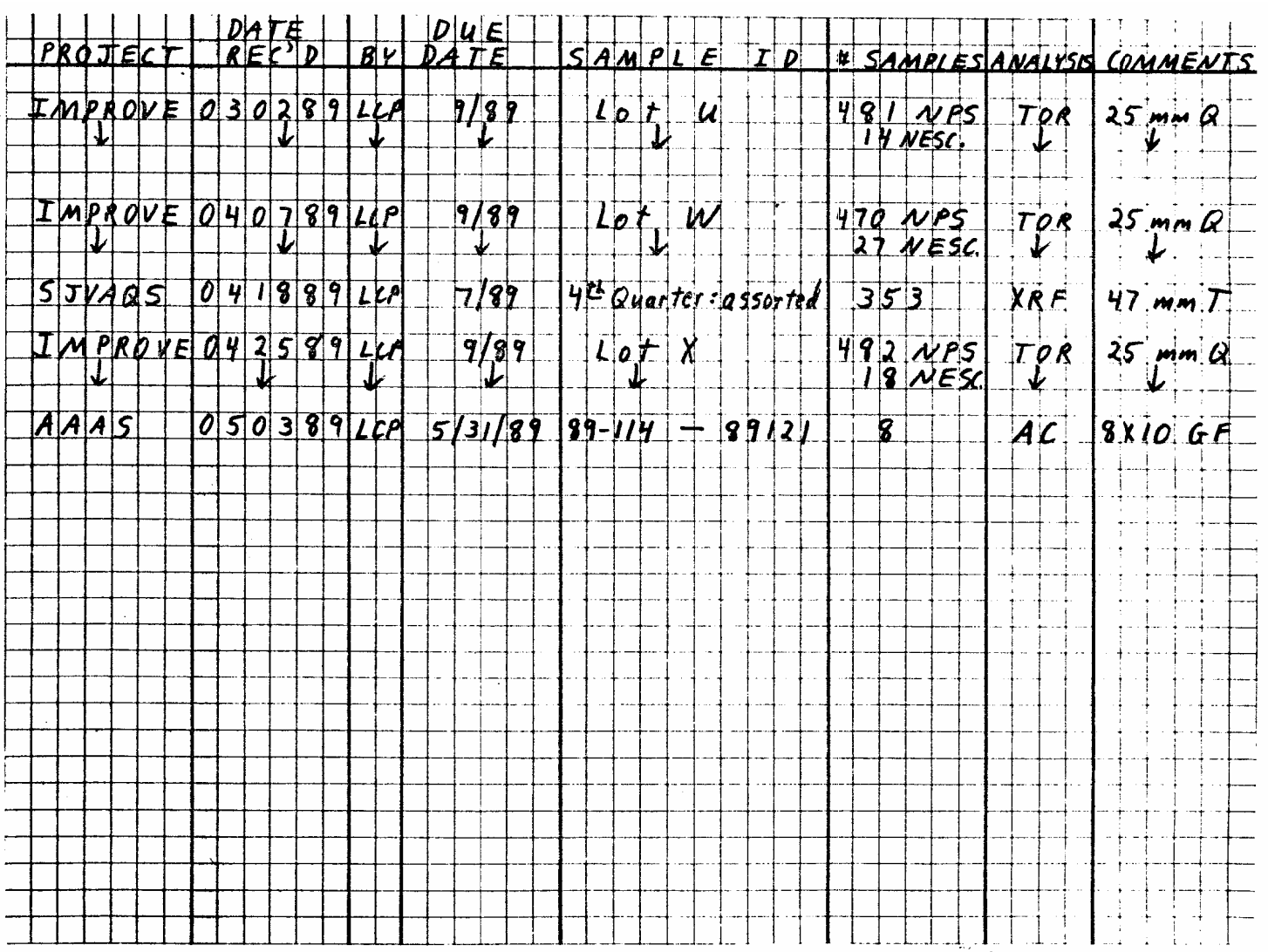
- Compressed air to supply oxygen to the FID, regulated to 10 psi by a metal diaphragm regulator

At least one backup cylinder per gas type should be kept on hand at all times. The calibration gases typically last for one year. The hydrogen, helium, and O_2/He mixture are typically replaced every four to six weeks. The compressed air is replaced every 4 to 5 days. All gases are replaced when the cylinder pressure drops below 500 psi.

2.4 Forms and Paperwork

All samples are logged into a receiving book and into a computerized database login file upon receipt at the laboratory. Refer to Figure 2-5 for the format of this logbook. A sample analysis list will be prepared by the laboratory supervisor indicating which samples will be analyzed and any special instructions.

As individual samples are analyzed, entries are made in the "Carbon Analyzer Logbook", as shown in Figure 2-6. As each analysis run is completed, the sample analysis list is marked with the date and analyzer number, as shown in Figure 2-7.



PROJECT	DATE REC'D	BY	DUE DATE	SAMPLE ID	# SAMPLES	ANALYSIS	COMMENTS
IMPROVE	030289	LCP	9/89	Lot U	481 NPS 14 NESC.	TOR	25 mm Q
IMPROVE	040789	LCP	9/89	Lot W	470 NPS 27 NESC.	TOR	25 mm Q
SJVAQS	041889	LCP	7/89	4th Quarter: assorted	353	XRF	47 mm T
IMPROVE	042589	LCP	9/89	Lot X	492 NPS 18 NESC.	TOR	25 mm Q
AAAS	050389	LCP	5/31/89	89-114 — 89121	8	AC	8X10 GF

Figure 2-5. DRI Air Analysis Logbook Format.

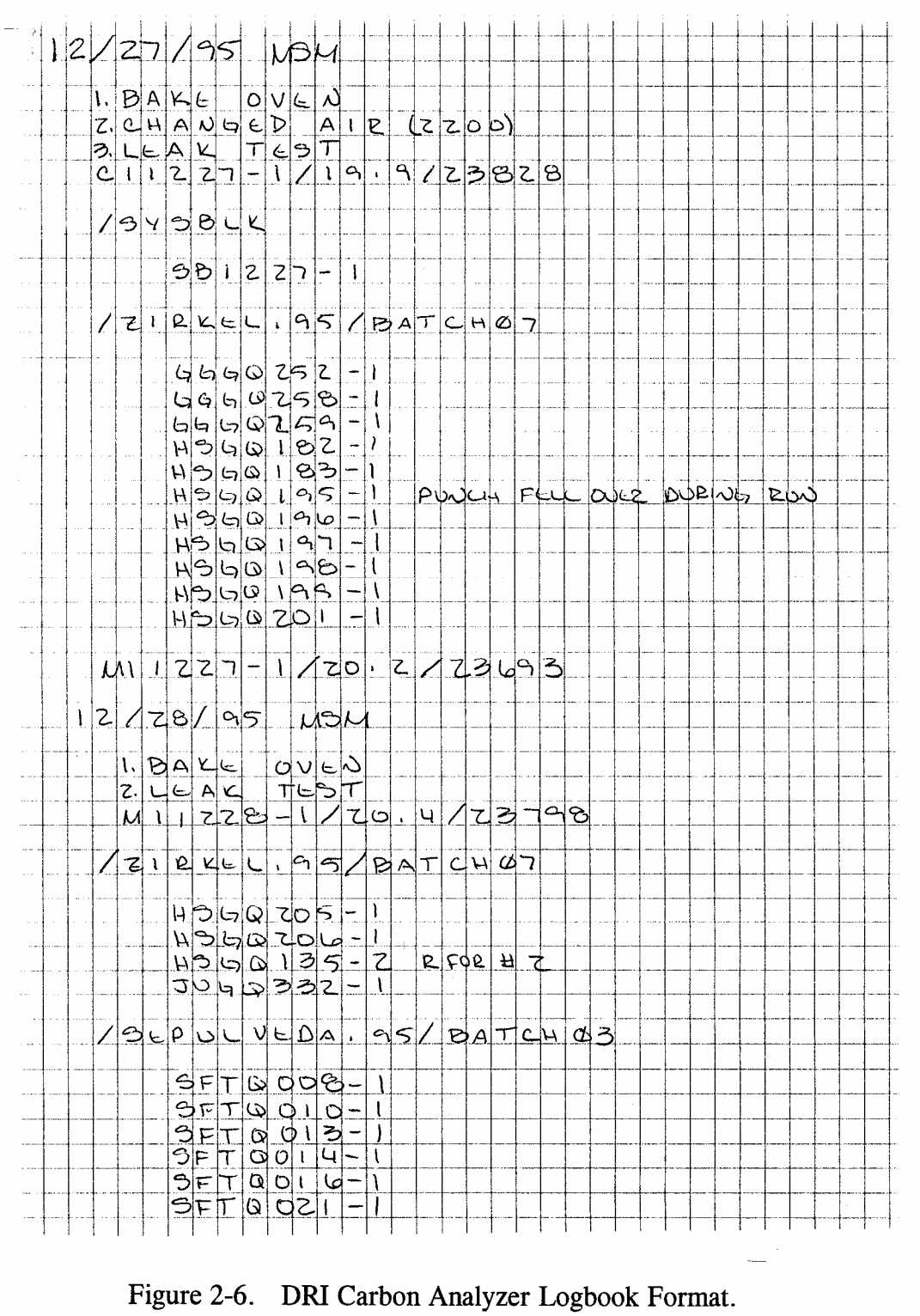


Figure 2-6. DRI Carbon Analyzer Logbook Format.

IMPROVE: Batch P3 Quartz

Date : Ø7/15/94

From : F.Divita

To : J.Chow
C.Frazier
B.Hinsvark
Carbon Lab

Analysis: OC/EC by TOR : 3ØØ samples, data in IMOETP3I.DBF

Sample Overview:

This analysis list covers samples from the NPS IMPROVE project. These are 3ØØ PM2.5 samples on 25 mm Quartz filters, including no lab blanks and 3 field blanks. These samples were collected with an IMPROVE sampler.

Analysis Overview:

Sample deposit area: 3.8 cm^2
Analysis start date: After LotO3
Analysis deadline : 6/16/94
Sample location : Back freezer

Analysis Details:

Carbon analysis data will be stored in the D:\IMPROVE\LOTP3 directory.

Filter	Description	OC/EC
P59916	GRCA1Ø4Ø594C1P	Y ____
P59917	GRCA1Ø4Ø594C1S	Y ____
P59918	GRCA1Ø4Ø594C2P	Y ____
P5992Ø	OKEF1Ø4Ø594C1P	Y ____
P59922	OKEF1Ø4Ø594C2P	Y ____
P59924	MEVE1Ø4Ø594C1P	Y ____
P59926	MEVE1Ø4Ø594C2P	Y ____
P59927	MEVE1Ø4Ø594C2S	Y ____
P59928	LAVO1Ø4Ø594C1P	Y ____
P5993Ø	LAVO1Ø4Ø594C2P	Y ____

Figure 2-7. Example DRI Carbon Analysis List.

3.0 CALIBRATION STANDARDS

3.1 Preparation, Ranges, and Traceability of Standards

Four standards are used in calibrating the carbon analyzers: 5% nominal CH_4 in He, 5% nominal CO_2 in He, KHP, and sucrose. Only the calibration gases are used on a daily basis as analyzer performance monitors. KHP and sucrose are used in conjunction with the two gases semiannually to establish the calibration curve of each analyzer.

The calibration gases are traceable to NIST standards. The gases are assayed for exact concentrations by the gas supplier to two decimal places. The assay value is obtained from the tag on the cylinders.

The KHP is dried at 110°C for two hours before dispensing. Transfer 0.3826 g of KHP into a glass 100 ml volumetric flask after the KHP has come to room temperature. Dilute to volume with 0.4 ml concentrated hydrochloric acid (HCl) and distilled deionized water (DDW). Mix the KHP thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration, nominally 1800 ppm carbon, is calculated by :

$$\left(\frac{\text{Actual g KHP}}{100\text{ ml}}\right)\left(\frac{96\text{ Carbon}}{204.23\text{ g KHP}}\right)\left(\frac{10^{-3}\text{ ml}}{\mu\text{l}}\right)\left(\frac{10^{6}\,\mu\text{g}}{\text{g}}\right)=\frac{\mu\text{g Carbon}}{\mu\text{l solution}}$$

The nominal 1800 ppm sucrose solution is prepared by transferring 0.428 g of sucrose into a glass 100 ml volumetric flask. Dilute to volume with DDW. Mix the sucrose thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration is calculated by:

$$\left(\frac{\text{Actual g Sucrose}}{100\,\text{ml}}\right)\left(\frac{144\text{ Carbon}}{342.31\text{ g Sucrose}}\right)\left(\frac{10^{-3}\text{ ml}}{\mu\text{l}}\right)\left(\frac{10^{6}\,\mu\text{g}}{\text{g}}\right)=\frac{\mu\text{g Carbon}}{\mu\text{l solution}}$$

To prepare a blank solution, add 0.4 ml of concentrated HCl to a glass 100 ml volumetric flask and dilute to volume with DDW. This acidified DDW is made fresh each time a 1800 ppm KHP stock solution is prepared.

No primary standards (NIST-traceable) currently exist for carbon analysis. Ideally, such standards should include a range of organic compounds from low to high molecular weights and with varying degrees of susceptibility to pyrolysis, as well as elemental carbon and carbonate compounds. Currently, KHP, sucrose, and the two calibration gases are used at DRI for calibration and system audit purposes.

3.2 Use of Standards

The calibration slopes derived from the two gases and the KHP- and sucrose-spiked filter punches are averaged together to yield a single calibration slope for a given analyzer. This slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation and methanator zones and the sensitivity of the FID. Note that the current calibration procedure is based only on the total carbon; currently no routine procedure exists to check the accuracy of the OC/EC split.

3.3 Typical Accuracy of Calibration Standards

The accuracy of the calibration standards is primarily limited by the accuracy of the calibration gas assays and by the accuracy of the preparation of the KHP and sucrose solutions. The calibration slopes determined by these four compounds historically differ by less than 5% on a given analyzer if sufficient care is taken during the calibration procedure (Section 5.1). Refer to Figure 3-1 for an example of plotted calibration curves.

4.0 PROCEDURES

4.1 Analyzer Start-Up

The following steps outline analyzer start-up:

- Check all gas cylinders' pressures; cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis. The cylinder pressure of new tanks should be recorded in **ALL** analyzer log books.

- Check that all gas delivery pressures are correct:

Hydrogen	--	17 psi	
Helium	--	15 psi	
Compressed air		--	10 psi
O_2/He mix	--	10 psi	
CH_4/He mix		--	10 psi
CO_2/He mix		--	10 psi

- Check that the FID is lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. If the FID is not lit (as immediately after the hydrogen or compressed air cylinders are changed), relight the flame by turning the H_2 rotameter to "100" and holding a butane lighter or match over the FID stack. A light pop indicates that the flame is lit. Verify that the flame remains lit by the tweezers test. Often the flame will not stay lit the first time, especially after the hydrogen cylinder is changed and air gets into the gas lines. If the FID is cold, allow at least 30 minutes at the high gas flow to pass before turning the H_2 rotameter to its correct setting.

- Check and readjust if necessary all gas flows at the analyzer. The correct readings are posted on each rotameter. Read through the center of the ball. If drastic adjustments are required on one analyzer, recheck that flows on the other three analyzers have not been affected.

- Double-click the **CARBON** shortcut to begin the carbon program.

- Insure that the sample port fitting is tight and that the thermocouple push rod is reasonably snug at the back fitting. If the push rod is loose, tighten the rear fitting NO MORE than 1/16 of a turn. Do not overtighten this fitting: a push rod that is too tight is difficult to operate smoothly, and will cause excessive wear of the Teflon ferrule.

- Perform a leak test on the system by flipping off the "From Oven" toggle valve. After the He-1 and He-2 rotameters settle to zero (if they don't reach zero in 2 minutes, see leak correction procedures below), flip off the "To Oven" toggle valve. This process pressurizes the oven and connecting tubing and then isolates the oven. After 30 seconds, flip on the "To Oven" toggle valve. If the He-1 rotameter float jumps more than 5 units, the system has an unacceptable leak. Correct the leak by checking the following items:

  - Check that the sample port fitting is tight.

  - Check that the push rod is snug.

  - If the system still leaks, disassemble the sample port fitting, wipe all threads and ferrules clean with a clean, dry Kimwipe, reassemble, and retry.

  - If the system continues to leak, check the integrity of the quartz oven and all tubing. Refer to the carbon analyzer troubleshooting manual for additional tips and procedures.

- When the system leak checks satisfactorily, select option 5 (manual mode) from the main menu of the Carbon program. This will result in the screen shown in Figure 4-2. While watching the He-1 and Cal Gas rotameters, select option 4 (toggle Carle valve). The He-1 rotameter should not change from zero, and the Cal Gas rotameter should momentarily dip down. While watching the same rotameters, select option 4 again. The He-1 rotameter should jump up momentarily and the Cal Gas reading should jump slightly. Behavior different than this indicates a leak in the calibration gas injection system which must be corrected before beginning any analyses. Refer to the carbon analyzer troubleshooting manual for additional information.

- Because calibration gas has been injected into the system by the above step, the system must be purged before continuing. Open the "From Oven" toggle valve to restore flow through the oven and wait at least two minutes to insure all calibration gas has progressed through the system.

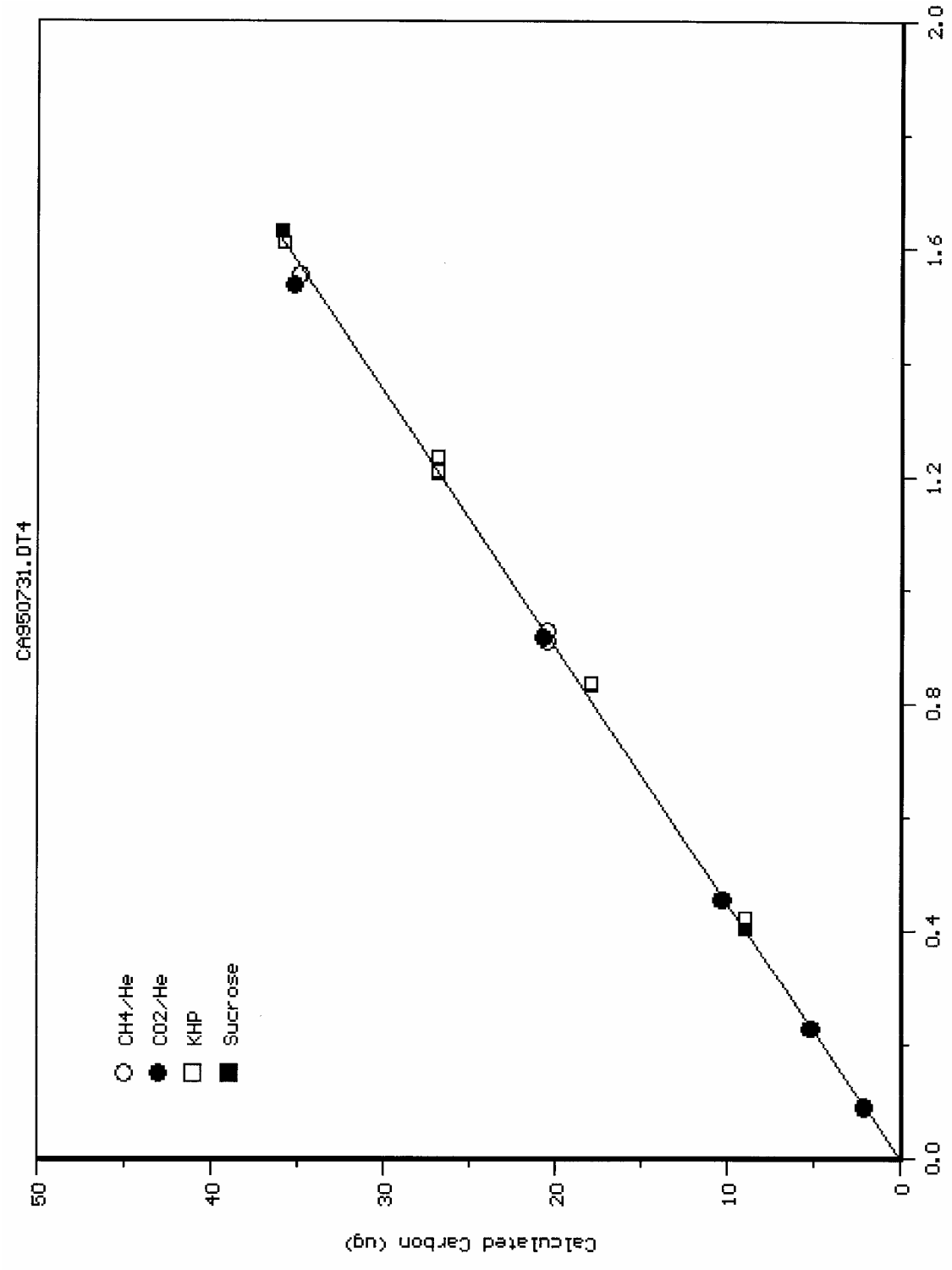


Figure 3-1. Example DRI Carbon Analyzer Calibration Curves.

- From the opening menu, select option 4; see Figure 4-1. After insuring that the thermocouple push rod is pushed into the combustion zone, type "Y" to begin baking the oven. The oven will be baked at 800°C for 10 minutes to insure that the system is clean before beginning analysis. This option is self-timed and will turn off the oven after 10 minutes has elapsed.

- Begin the daily entry in the carbon analyzer logbook. Entries should follow the format in Figure 2-6.

- Use the sample tweezers to remove a Kimwipe. Wipe the sample tweezers, petri dish, and punching tool with clean Kimwipes, taking care not to contact the cleaned surfaces with fingers or other dirty items.

- Insure that the printer has enough paper for the day and that the printer toner cartridge is producing legible printing.

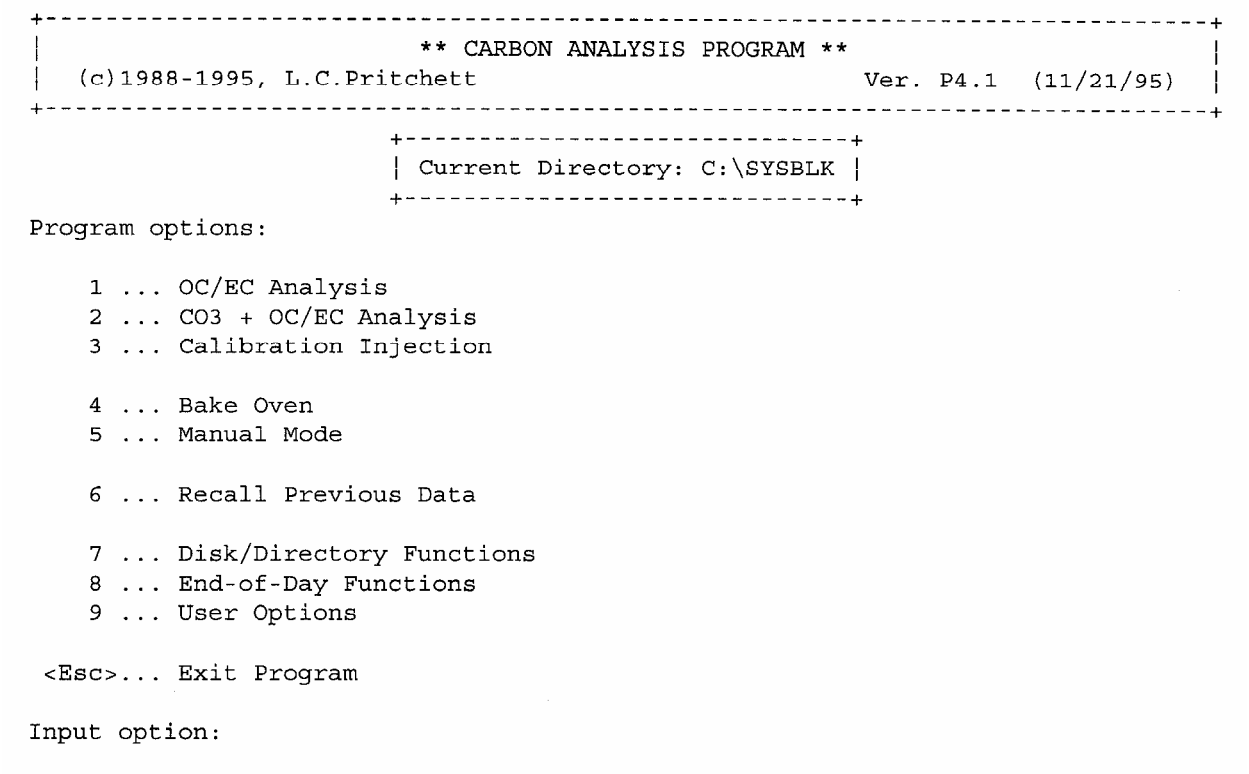


Figure 4-1. DRI Carbon Program Main Menu.

- Press **<Esc>** to return the Carbon program to the main menu. Select option 3 (calibration run) to begin the morning calibration injection. Note: the program will automatically change to the **\CALIB** subdirectory during the calibration run, and will return to the current subdirectory when the calibration run is done. Select He/O_2 carrier gas (option 2). Select either CO_2 or CH_4 calibration gas type as the same gas used the previous afternoon (check the analyzer logbook). For any given day, one gas will be used in the morning and the other in the afternoon. By using the same gas in the morning as was used the previous afternoon, the calibration gas used in the morning will be rotated on a regular schedule.

- The computer will create a sample ID based on the gas type, current date, and run number. This ID should be entered in the analyzer logbook (see Figures 4-3 and 2-6). Press **<N>** in response to the purge option to begin the calibration run.

- Insure that the printer is on-line.

- When the elapsed time reaches 60 seconds (Figure 4-4), flush the 1000 ml syringe with the appropriate calibration gas three times. A low pitch warning tone will sound at 84 seconds (the number of beeps corresponds to the carbon analyzer number). When the analysis start tone sounds at 90 seconds, inject 1000 ml of the calibration gas into the injection port before the oven. The rest of the analysis is automatic.

- If the calibration injection is late or missed, press **<Esc>** to abort the run. Restart the calibration run by selecting option 3 from the main menu.

- When the analysis is complete, a tabular and graphical printout similar to Figures 4-5 and 4-6 will be generated. From the tabular printout locate the calibration peak counts and the calculated µg C/filter. Record these values in the logbook as in Figure 2-6. The calibration peak counts should be above 20,000 counts. Check the µg C value for the calibration gas against those posted on each carbon analyzer.

```
Oven:  62 °C       Reflectance: 1.658 V      Transmission: NA         FID: 0.100
--------------------------------------------------------------------------------
Current settings:  Temperature : 5 °C
                   Front valves: Off   Back valves: Off   Carle valve: Inject
                   Fan         : Off   Pushrod    : Undef
--------------------------------------------------------------------------------

Manual control options:

    1 ... Set Oven Temperature

    2 ... Toggle Front Valves
    3 ... Toggle Back Valves
    4 ... Toggle Carle Valve

    5 ... Toggle Cooling Fan

    6 ... Move Pushrod

    7 ... Reset All

 <Esc>... Exit Option

Input option:
```

Figure 4-2. DRI Carbon Program Manual Control Menu.

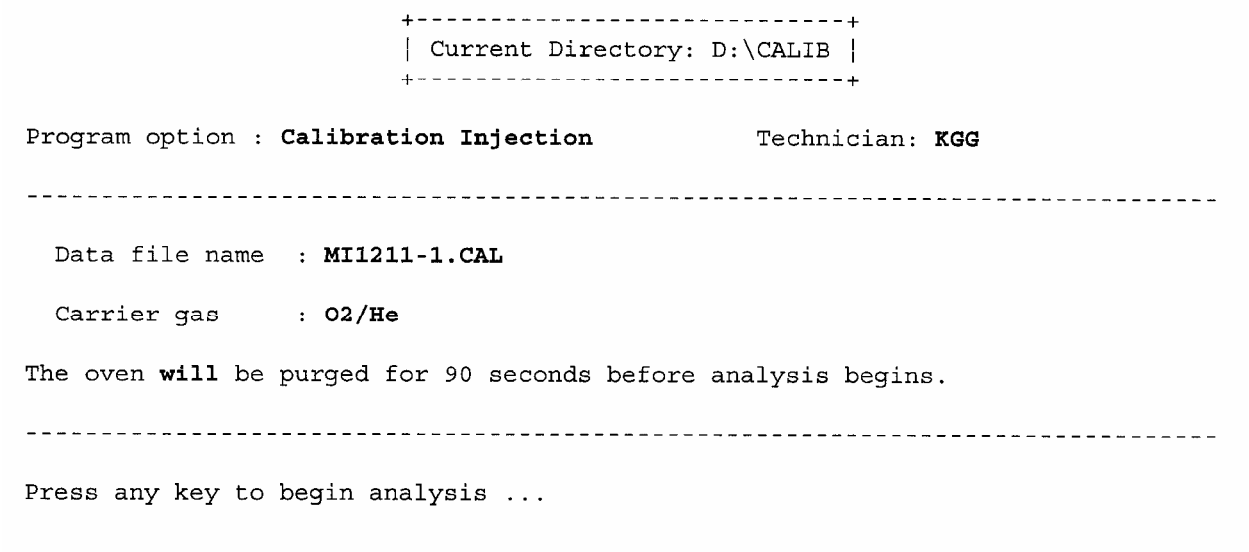


Figure 4-3. DRI Carbon Program Screen Before Starting Calibration Run.

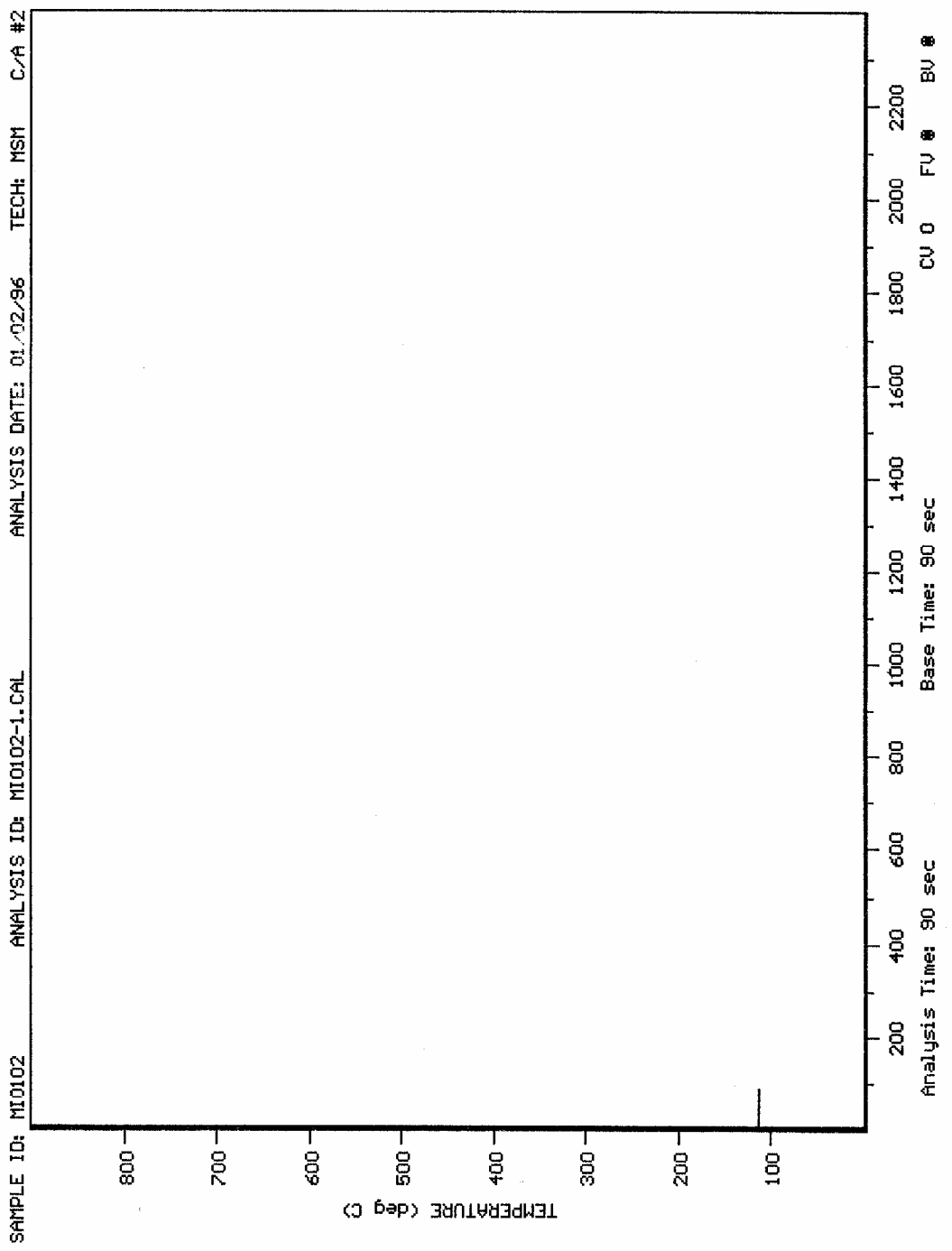


Figure 4-4. DRI Carbon Program Screen at 90 Seconds.

```
                              CARBON ANALYSIS RESULTS
Analyzer #4                                                    Technician: KGG
-------------------------------------------------------------------------------

Analysis ID      : MI1211-1.CAL
Sample ID        : MI1211
Carrier gas      : Oxygen/Helium mix

Analysis         : 12/11/95  09:33        Calculation      : 01/03/96  14:57
-------------------------------------------------------------------------------
Anal program ver: P4.1  (11/21/95)        Parm file ver    : D4.04  (11/21/95)
Calib. slope     : 22.25 ug C/peak ratio   Baseline time    :   90 sec
Calib. intercept:  0.00 ug C               Baseline window  :    1 counts
Reflectance unc.:    10 counts             Transmission unc.:   10 counts
Sample transit   :    28 sec              Calib. transit   :   45 sec
-------------------------------------------------------------------------------
Calibration peak area: 23736 counts
Initial FID baseline :   205 counts
-------------------------------------------------------------------------------
                     Peak Area                      Carbon
  Peak #1         : 21508 counts    20.16 ug C/injection

*******************************************************************************

  Calculated Carbon:
       20.2 ug C/injection
```

Figure 4-5. DRI Carbon Program Tabular Printout, Calibration Run.

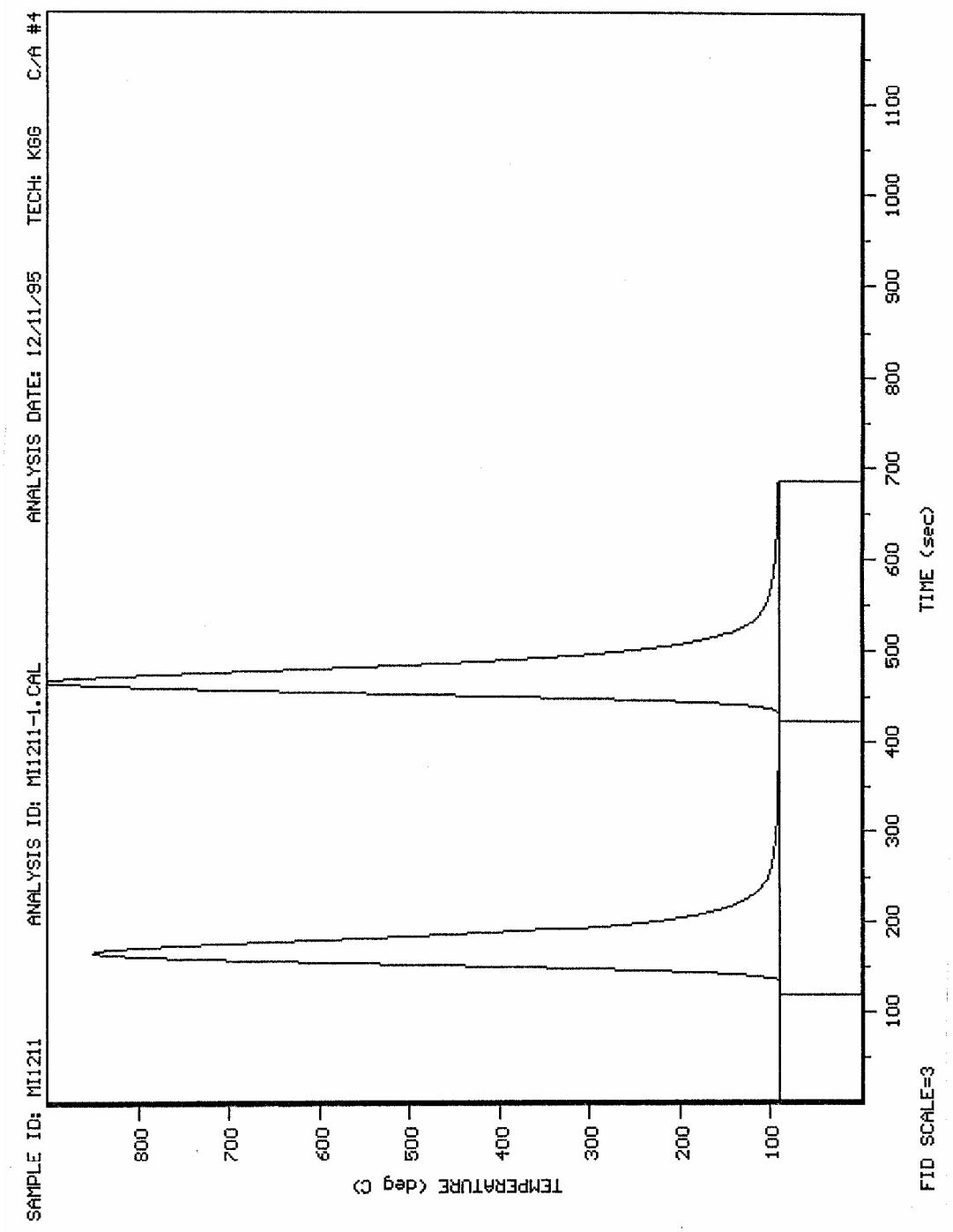


Figure 4-6. DRI Carbon Program Thermogram Printout, Calibration Run.

If the calibration result is unsatisfactory, follow the steps below until a satisfactory result is obtained:

1. Repeat the calibration using the same calibration gas under a He only atmosphere.

2. Perform a full "Leak Test" as described in Section 4.1 in order to determine if a gas leak exists. If this test fails, correct the problem and proceed to Step 3 (the most common problem is a poorly placed port fitting).

3. Repeat the calibration using the same calibration gas but under a He/O_2 atmosphere.

4. Repeat the calibration using the other calibration gas under a He/O_2 atmosphere.

5. If the calibration still does not pass and if possible, consult the laboratory manager for instructions.

- From the main menu of the Carbon program, select option 7 to change to the appropriate subdirectory for the samples to be analyzed. The new subdirectory name, if valid, will be displayed at the top on the screen.

- Based on the analysis list for the day, retrieve the samples to be analyzed from the sample freezer and place in a cooler with blue ice. Place the cooler in the instrument room.

4.2 Routine Operation

Routine analysis procedures depend on whether or not carbonate carbon will be determined before OC/EC analysis. The procedures are different for these two options.

4.2.1 Routine OC/EC Analysis

- Pull the push rod back to the idle zone of the quartz oven (approximately half way between the sample port and the heating element). Allow the boat/push rod to cool until the reading on the front of the analyzer reaches 50°C or less. Do not pull the boat into the sample loading zone when the boat is still hot as the heat will damage the Teflon ferrules of the sample port fitting.

- Insure that the petri dish, tweezers, and punching tool are thoroughly wiped clean with a dry KimWipe.

- Based on the analysis list, remove the sample to be analyzed from the sample cooler.

- Remove the filter from the PetriSlide or petri dish with tweezers, handling the filter only by the edge. Place the filter on the glass petri dish and remove a sample punch by pushing down gently on the punching tool. Rocking the punching tool slightly will insure that the punch is complete severed. Try to remove the punch from the edge of the deposit to avoid wasting the filter, but try to avoid areas of non-uniform deposits. Leaving the sample punch in the punching tool, place the punching tool on a clean Kimwipe. Return the filter to the PetriSlide or petri dish.

- Record the filter ID in the analyzer log book (Figure 2-6).

- After the boat has cooled to 50°C or less, loosen the sample port fitting carefully with a wrench. NOTE: avoid exerting any sideways pressure on the quartz oven. Try to confine the wrench pressure to only rotational torque. Loosen the front fitting before attempting the rear fitting. Slide the sample port fitting forward.

- Pull the boat back until it is centered in the sample port, taking care that the small stainless steel "ear" holding the boat to the push rod does not catch on the sample port opening and bend. If the "ear" does bend, carefully bend it back into position with tweezers or small clean pliers.

- Using the tweezers, push the bottom of the punch in the boat forward so that the top of the punch can be accessed. Remove the punch and place it on the top of the analyzer.

- Push the top of the sample punch with tweezers to rotate the punch within the punching tool. Remove the sample from the punching tool by grasping the bottom edge with the tweezers. Place the punch in the sample boat. Generally, the punch must be inserted sideways into the boat and then turned so the punch wedges itself facing forward. Push the punch forward until it is seated against the front of the slot in the boat.

- Push the push rod forward until the boat is located in the idle zone of the quartz oven (Figure 2-4). Slide the sample port fitting back until it is centered over the sample port and tighten firmly by hand. **DO NOT** tighten with a wrench. As before, avoid exerting any sideways pressure on the quartz oven.

- Select option 1 of the main menu of the Carbon program (Figure 4-1). Input the full sample ID. NOTE: the program will automatically place the computer into Caps Lock mode. After verifying the sample ID, enter the run number (1-9). The run number must correspond to the number of punches removed from the filter; for example, if the punch placed in the quartz boat is the third punch taken from the filter, the run number must be "3". Replicate runs are designated simply by the appropriate punch number (usually "2"). Note: the program creates a file name using the last six characters of the sample ID plus the run number; if the program finds another file with the same name, it will request that a new run number be input so the existing file will not be overwritten.

- Input the appropriate punch size (normally 0.536 cm^2) and filter deposit area (defined on the sample analysis list, Figure 2-7). Note that pressing **<Return>** is not necessary. Also note that if a mistake is made during input of analysis data pressing **<Esc>** will allow the option to be aborted and restarted.

- Enter any analysis flag options. A list of valid choices is presented on screen.

- Answer the purge question (Figure 4-7) by pressing **<Y>**. The sample oven must be purged with He for two minutes to remove all oxygen before the analysis begins. This question may be answered **<N>** if the run was aborted and is being restarted and the sample port was not opened.

- A data verification screen will appear (Figure 4-8). When all data is deemed correct, press any key except **<Esc>** to start the analysis program. If corrections are necessary, press **<Esc>** to clear the screen and return to the main menu.

- Using a small piece of clear tape, attach the previous sample punch to its thermogram, insuring that the deposit side is up.

- Wipe the tweezers, petri dish, and punching tool with clean Kimwipes.

- Replace the PetriSlide or petri dish containing the filter into the styrofoam cooler.

- The program will purge the oven with He for 90 seconds, after which data collection will begin. Readings are collected for 90 seconds to establish baselines. At 84 seconds, a warning tone will sound (the number of beeps corresponds to the analyzer number). At 90 seconds the analysis start tone will sound. At that time, push in the thermocouple/push rod until the stop is against the back fitting. While watching the punch, pull the push rod back 1-2 mm to physically decouple the push rod from the boat. If the boat slides back, immediately push the thermocouple back in and try again. The boat cannot be physically attached to the push rod during analysis, since the expansion of the thermocouple as the sample is heated will push the sample punch closer to the laser rod and cause erroneous laser signals.

- All physical adjustments must be made within 10 seconds: the laser baseline is calculated between 100 and 110 seconds analysis time. If the sample is not correctly positioned at the end of 10 seconds, press **<Esc>** to abort the program, pull the boat back to the idle zone, and restart the program. Decoupling the boat is most important for a meaningful laser signal.

```
          +----------------------------------------+
          | Current Directory: D:\MINTEK.94\BATCH09 |
          +----------------------------------------+

Program option : OC/EC Analysis                    Technician: KGG

Enter full sample ID: NEL015Q Is this okay? Y

Enter run/punch number for this sample (1-9): 1

-------------------------------------------------------------------------------
Punch size options:

    1 ... 0.536 cm²
    2 ... 0.484 cm²
    3 ... 1     cm²
    4 ... other

Input option: 1

-------------------------------------------------------------------------------
Filter deposit area options:

    1 ...   1   cm²
    2 ...   3.8 cm²
    3 ...   6.4 cm²
    4 ...   8.3 cm²
    5 ...  13.8 cm²
    6 ...   7.1 cm²
    7 ... other

Input option: 7

-------------------------------------------------------------------------------
Analysis flag options:

    1 ... no problems
    2 ... blank filter (field blank, transport blank, etc.)
    3 ... sample dropped
    4 ... filter media damaged
    5 ... sample deposit damaged
    6 ... inhomogeneous sample deposit
    7 ... foreign substance(s) on deposit
    8 ... wet sample

Input option: 1

-------------------------------------------------------------------------------
Does the oven need to be purged? Y
```

Figure 4-7. DRI Carbon Program Before Starting Regular Analysis Run.

```
          +----------------------------------------+
          | Current Directory: D:\MINTEK.94\BATCH09 |
          +----------------------------------------+

Program option : OC/EC Analysis                    Technician: KGG

-------------------------------------------------------------------

Sample ID          : NEL051Q

  Data file name   : EL015Q-1.OEC

  Punch size       : 0.536 cm²

  Filter deposit   : 17.3 cm²

  Analysis flag    :

The oven will be purged for 90 seconds before analysis begins.

-------------------------------------------------------------------

Press any key to begin analysis ...
```

Figure 4-8. DRI Carbon Program Data Entry Verification Screen.

- The program will proceed automatically from this point without further operator intervention. At the end of the program, data is saved to disk, split times are calculated, carbon peaks are integrated, and tabular and graphical printouts are produced. When the printer begins, the push rod may be pulled back to the idle zone to begin cooling.

- Examine the tabular printout (Figure 4-9) to insure the calibration peak counts are within specifications (see Section 4.1). Examine the thermogram (Figure 4-10) for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis (Section 6.5.1). Finally, examine the laser signal at the end of the run. Drooping of the laser signal as the temperature is dropping is an indication that the boat was coupled to the push rod and that the sample should be rerun. If all aspects of the analysis appears correct, select the appropriate analysis flag from the screen that appears at the end of the run (Figure 4-11). Also, mark the analysis date on the sample analysis list. If a problem is found, indicate the problem in the analyzer log book and rerun the sample.

- Repeat the above steps for additional sample runs.

4.2.2 System Blanks

System blanks are run at the beginning of each week. Follow the steps outlined in Section 4.2.1 with the following exceptions:

- Use option 7 from the main menu to change to the **\SYSBLK** subdirectory.

- Go through all the steps for a normal analysis, with the exception that the punch from the previous analysis is not removed. Open the sample port, pull the boat back into the loading zone, and without touching the existing punch push the boat forward into the idle zone, seal the sample port, and proceed with the analysis.

- Use an ID number derived from the current date: e.g., **SB0412** for April 12.

- Use a punch size of 1.0 cm^2 and a 1.0 cm^2 deposit area.

- Calculated carbon concentrations should not be more than 0.2 µg total carbon. Values greater than this warrant additional system blanks. Samples may not be analyzed until the system blank is < 0.2 µg total carbon.

4.2.3 Carbonate Analysis

- Follow the steps under Section 4.2.1 until the sample punch is loaded into the boat. Pull the boat BACK until the punch is centered under the acid injection port, taking care that the "ears" holding the boat to the push rod are not bent in the process.

CARBON ANALYSIS RESULTS

Analyzer #4 Technician: KGG

Analysis ID : EL051Q-1.OEC
Sample ID : NEL051Q
Punch area : 0.536 cm2
Deposit area : 17.30 cm2

Analysis : 12/11/95 10:23 Calculation : 01/03/96 15:11

Anal program ver: P4.1 (11/21/95) Parm file ver : D4.04 (11/21/95)
Calib. slope : 22.25 ug C/peak ratio Baseline time : 90 sec
Calib. intercept: 0.00 ug C Baseline window : 1 counts
Reflectance unc.: 10 counts Transmission unc.: 10 counts
Sample transit : 28 sec Calib. transit : 45 sec

Calibration peak area: 23577 counts
Initial FID baseline : 205 counts
Final FID baseline : 206 counts

	Reflect Split Time	Laser	FID Split Time
Lower split :	1348 sec	1661 counts	1376 sec
Regular split:	1350 sec	1678 counts	1378 sec
Upper split :	1352 sec	1694 counts	1380 sec

	Peak Area	Carbon	
OC Peak #1 :	356 counts	0.63 ug C/cm2	10.84 ug C/filter
OC Peak #2 :	1848 counts	3.25 ug C/cm2	56.29 ug C/filter
OC Peak #3 :	3681 counts	6.48 ug C/cm2	112.12 ug C/filter
OC Peak #4 :	2390 counts	4.21 ug C/cm2	72.80 ug C/filter
Lower pyro'd OC :	533 counts	0.94 ug C/cm2	16.23 ug C/filter
Reg. pyro'd OC :	602 counts	1.06 ug C/cm2	18.34 ug C/filter
Upper pyro'd OC :	673 counts	1.18 ug C/cm2	20.50 ug C/filter
EC Peak #1 :	3310 counts	5.83 ug C/cm2	100.82 ug C/filter
EC Peak #2 :	265 counts	0.47 ug C/cm2	8.07 ug C/filter
EC Peak #3 :	58 counts	0.10 ug C/cm2	1.77 ug C/filter

****

	VOC	Regular OC	High Temp OC	Regular EC	High Temp EC	TC	
Lower split :	0.6	15.5	14.9	5.5	0.6	21.0	ug C/cm2
	10.8	268.3	257.4	94.4	9.8	362.7	ug C/filter
Regular split:	0.6	15.6	15.0	5.3	0.6	21.0	ug C/cm2
	10.8	270.4	259.5	92.3	9.8	362.7	ug C/filter
Upper split :	0.6	15.8	15.1	5.2	0.6	21.0	ug C/cm2
	10.8	272.6	261.7	90.2	9.8	362.7	ug C/filter

****

OC/TC: 0.75
EC/TC: 0.25
OC/EC: 2.93

Figure 4-9. DRI Carbon Program Tabular Printout, OC/EC Run.

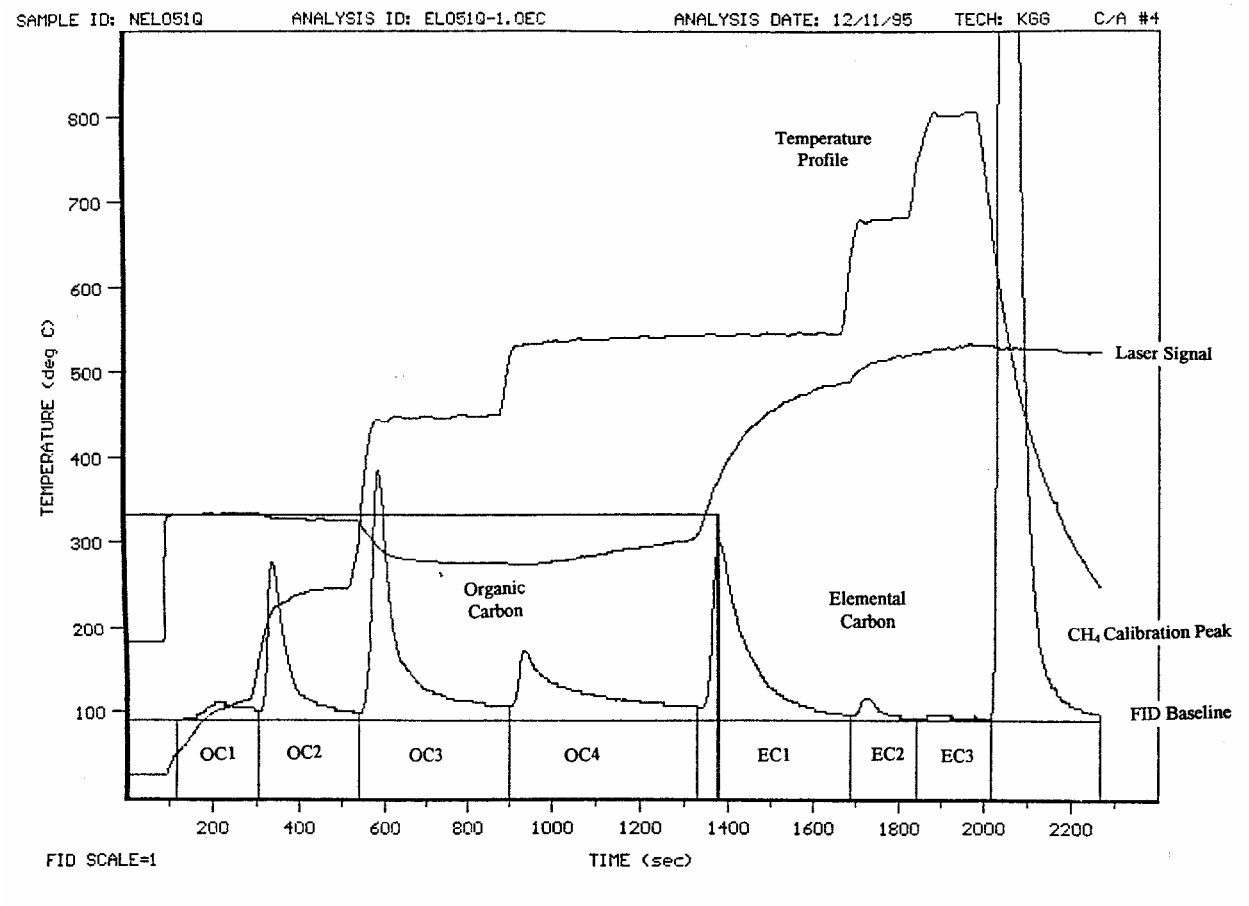


Figure 4-10. DRI Carbon Program Thermogram Printout, OC/EC Run.

```
Analysis validation values:

          Initial FID baseline :  23577 counts
          Final FID baseline   :    205 counts
          Calibration peak     :    206 counts

          Current analysis flag:
--------------------------------------------------------------------------------
Analysis flag options:

    1 ... No Problems
    2 ... Error in Sample ID
    3 ... Error in Deposit or Punch Area
    4 ... Temperature Suspect
    5 ... FID Suspect
    6 ... Laser Suspect
    7 ... Miscellaneous Problem
    8 ... Invalid

    9 ... Recall Thermogram for Review

 <Esc>... Exit Option (accept current flag)

Input option:
```

Figure 4-11. DRI Carbon Program Analysis Flags Menu.

- Select option 2 from the main menu (Figure 4-1). Enter the sample ID, run number, punch size, and filter size. Select the purge option and start the analysis program.

- At 60 seconds elapsed analysis time, flush the 25 ml syringe with 0.4 M hydrochloric acid (HCl) into a waste beaker. When the start tone sounds at 90 seconds elapsed time, eject 20 ml HCl onto the filter punch, insuring that the needle bevel is turned toward the punch and that the needle tip is touching the top of the punch.

- When the analysis is underway, flush the syringe with distilled water to prevent corrosion of the syringe plunger.

- After the carbonate analysis is completed, a tabular summary and a copy of the graph will be printed (similar in format to Figures 4-5 and 4-6). The program will automatically cycle into the normal OC/EC analysis, using the same sample ID. Push the sample boat into the punch drying area (about 1 cm from the first coil of the sample oven; see Figure 2-4). If the sample punch has tipped over during the carbonate analysis, open the sample port, reorient the punch, close the port, and proceed with drying the punch. Heat from the oxidation oven will dry the sample in this position without prematurely baking carbon from the sample; the sample temperature should not exceed 42°C. When the punch appears to be dry (wait at least 5 minutes), start the OC/EC analysis.

4.3 Analyzer Shut-Down

After the final sample for the day is analyzed, shut down the analyzers by:

- Leave the last analyzed punch in the boat with the boat positioned in the heating zone.

- Select option 3 to begin the calibration gas injection routine. Follow the injection procedures outlined in Section 4.1, with the exceptions that a He-only atmosphere is used during the afternoon check and the alternate calibration gas is used.

- When the analysis is completed, record the calibration peak counts and calculated injection calibration in the logbook. Any values outside the ranges defined in Section 4.1 should be investigated and rerun. Because low values from the end-of-day calibration could potentially invalidate the entire day's runs, any deviation from the accepted ranges must be noted and the cause identified.

- Select option 8 (End-of-Day Functions) from the main menu (Figure 4-1). A submenu will appear with options for daily summary printouts and automated backup of all new data files (Figure 4-12).

- Select option 1 from the submenu and follow all on-screen directions. A single page summary will be printed for each subdirectory (each project) containing samples analyzed during that day (Figure 4-13). The End-of-Day Functions submenu will reappear when the printing is done.

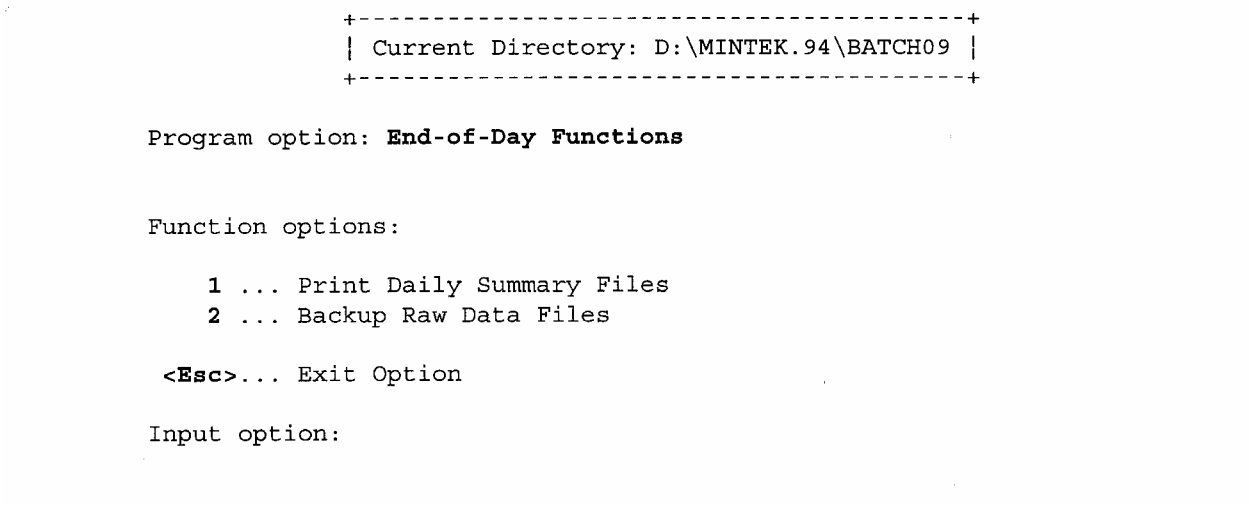


Figure 4-12. DRI Carbon Program End-of-Day Functions Menu.

DAILY CARBON ANALYSIS SUMMARY
****

Analyzer : #4
Analysis Date : 12/11/95
Directory : D:\MINTEK.94\BATCH09

Original Analyses : 10
Reruns/Replicates : 0

Analysis ID	Sample ID	Flag	OC1 (ug/f)	OC2 (ug/f)	OC3 (ug/f)	OC4 (ug/f)	POC (ug/f)	EC1 (ug/f)	EC2 (ug/f)	EC3 (ug/f)	Deposit Area	Tech
EL051Q-1.OEC	NEL051Q		-99.00	10.84	56.29	112.12	72.80	18.34	100.82	8.07	1.77	17.30	KKO
EL052Q-1.OEC	NEL052Q		-99.00	10.42	52.03	109.02	75.73	26.44	118.83	7.43	0.37	17.30	MSM
ELR03Q-1.OEC	NELR03Q		-99.00	32.14	39.50	54.43	47.17	44.24	57.21	23.09	2.25	17.30	MSM
ELR04Q-1.OEC	NELR04Q		-99.00	28.12	42.13	57.22	47.65	52.74	61.60	20.42	2.45	17.30	MSM
ELR15Q-1.OEC	NELR15Q		-99.00	22.25	30.11	48.74	27.84	17.84	36.66	13.31	0.00	17.30	MSM
ELR16Q-1.OEC	NELR16Q		-99.00	23.65	36.28	49.66	32.09	25.49	47.77	14.15	0.18	17.30	MSM
OLF15Q-1.OEC	OLF15Q		-99.00	106.45	201.63	382.75	294.97	248.26	769.83	21.07	7.00	17.30	MSM
OLF16Q-1.OEC	OLF16Q		-99.00	82.42	179.69	333.19	257.24	211.95	680.76	22.26	7.05	17.30	MSM
OLF43Q-1.OEC	OLF43Q		-99.00	30.11	94.55	172.90	131.19	48.64	262.26	22.13	3.84	17.30	MSM
OLF44Q-1.OEC	OLF44Q		-99.00	26.94	70.64	153.11	118.14	30.43	184.84	24.20	5.83	17.30	MSM

Figure 4-13. DRI Carbon Program Daily Summary Printout.

- Select option 2 from the submenu and follow all on-screen directions. Pre-formatted LS-120 super disk must be available before this option is selected. The program will automatically copy to the floppy disk all files created or modified since the last backup in each subdirectory selected that day. Begin with the floppy disk used the previous day. If the floppy disk is filled, the program will prompt for a new formatted disk. When all files are copied to the floppy disks, the End-of-Day Functions submenu will reappear. Press **<Esc>** to return to the main menu.

- Label the floppy disks in the following format:

Analyzer# CARBON BACKUP startdate-enddate

For example, for a disk containing data files for analyses run on September 1, 2, and 3, the label would be written:

C/A# 1 CARBON BACKUP 09/1/00-09/1/00

- Place full disks in the storage boxes located in the laboratory supervisor's office. Leave partially filled disks (there should be no more than one per analyzer) in the "Active Floppies" box in the Carbon Laboratory.

- Press **<Esc>** to end the Carbon program. This is necessary because when the Carbon program ends, it sets the analyzer valves such that oxygen is flowing through the MnO_2 catalyst, allowing some regeneration of the catalyst overnight.

- Remove the printouts and attach them to a manila folder labeled with the date and analyzer number. Place on the lab supervisor's desk for Level I validation (Section 6.5).

- Leave the computers and analyzers on overnight unless the potential for power outages or surges exists. You may turn the monitors off or leave them on. **DO NOT** start a screensaver program. This will interfere with the nightly backup program.

- Make a final check of the gas cylinder pressures to insure that gas flow, especially the compressed air, will continue until someone will be available to check them again.

- Put the samples and blue ice in the sample cooler back into the sample storage freezer and lock the freezer.

- If the 25 ml syringe was used for carbonate analysis, thoroughly rinse the syringe with distilled water and tightly cap all solutions.

- Lock the carbon analysis room.

4.4 Abbreviated Operational Checklist

4.4.1 Start-Up:

- Check all gas cylinders' pressures and delivery pressures.
- Check that all FIDs are lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. Relight if necessary.
- Check and readjust if necessary all gas flows at the analyzer.
- Turn on the computer monitor.
- Insure that the date on the computer is current.
- Double-Click the **CARBON** icon to begin the carbon program.
- Insure that the sample port fitting is tight and that the thermocouple push rod is reasonably snug at the back fitting.
- Perform a leak test, involving isolating the oven and operating the Carle valve.
- Purge the system of calibration gas injected by the above step.
- From the opening menu, select option 4 to bake the oven for 10 minutes.
- Begin the daily entry in the carbon analyzer logbook.
- Wipe the sample tweezers, petri dishes, and punching tool with clean Kimwipes.
- Insure that the printers have enough paper for the day and that the toner cartridge is producing legible printing.
- Perform the morning calibration injection by selecting option 3 and He/O_2 carrier gas (option 1). When the analysis is complete, record the calibration peak counts and injection concentration. Insure that these values are within their proper ranges.
- Change to the appropriate subdirectory for the samples to be analyzed.
- Retrieve the samples to be analyzed from the sample freezer.

4.4.2 Routine OC/EC Analysis

- Pull the push rod back to the idle zone of the quartz oven and allow the boat/push rod to cool.
- Insure that the tweezers, petri dish, and punching tool are wiped clean.

- Based on the analysis list, remove the sample to be analyzed from the sample cooler.
- Remove a sample punch from the filter.
- Record the filter ID in the analyzer logbook, along with any comments on the condition of the deposit or any other conditions which might affect analysis results.
- After the boat has cooled to 50°C or less, remove the previously analyzed sample punch and load the current sample punch.
- Begin the analysis by selecting option 1 from the main menu of the Carbon program and inputting the sample ID, run number, punch size, and filter deposit area.
- Push the sample into the heated zone at 90 seconds, insuring that the boat is not physically coupled to the push rod.
- Using a small piece of clear tape, attach the previous sample punch to its thermogram, insuring that the deposit side is up.
- Clean the tweezers, petri dish, and punching tool.
- Replace the PetriSlide or petri dish containing the filter into the sample cooler.
- At the end of the analysis, the push rod should be pulled back to the idle zone to begin cooling.
- Examine the thermogram for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis. Examine the tabular printout to insure the calibration peak counts are within specifications (see Section 4.1). Finally, examine the laser signal at the end of the run. Rerun any deviants immediately. Indicate successful analyses on the sample analysis list.
- Repeat the above steps for additional samples.

4.4.3 System Blanks (run first each Monday):

- Change to the **\SYSBLK** subdirectory.
- Go through all the steps for a normal analysis, with the exception that the punch from the previous analysis is not removed. Open the sample port, pull the boat back into the loading zone, and without touching the existing punch push the boat forward into the idle zone, seal the sample port, and proceed with the analysis.
- Use an ID number derived from the current date: e.g., **SB0412**.

- Calculated carbon concentrations should not be more that 0.2 µg carbon. Values greater than this warrant an additional system blank.

4.4.4 Carbonate Analysis:

- Follow the steps under Routine Analysis until the sample punch is loaded into the boat. Pull the boat BACK until the punch is centered under the acid injection port.
- Select option 2 from the main menu. Enter the sample ID, run number, punch size, and filter size. Select the purge option and start the analysis program.
- At 90 seconds elapsed time, eject 20 ml HCl onto the filter punch.
- Flush the syringe with distilled deionized water between samples.
- Continue the normal OC/EC analysis when the carbonate cycle is complete.

4.4.5 Analyzer Shut-Down:

- Leave the last analyzed punch in the boat with the boat positioned in the heating zone.
- Select option 3 to begin the calibration gas injection routine. Follow the injection procedures outlined in the Start Up section with the exception that a He only atmosphere is used.
- When the analysis is complete, record the calibration peak counts and calculated injection calibration in the logbook. Any values outside the ranges defined in Section 4.1 should be investigated and rerun.
- Print summaries of the day's analyses.
- Backup the day's data files.
- Remove the printouts and attach them to a manila folder labeled with the date and analyzer number. Place on the lab supervisor's desk.
- Turn off the computer monitors.
- Make a final check of the gas cylinder pressures.
- Put the samples and blue ice in the sample cooler back into the sample storage freezer and lock the freezer.
- If the 25 ml syringe was used for carbonate analysis, thoroughly rinse the syringe with distilled water and tightly cap all solutions.
- Lock the carbon analysis room.

5.0 QUANTIFICATION

5.1 Calibration procedures

The calibration procedures for the carbon analyzers are of three types: the end-of-run calibration peak, the manual calibration injections of CH_4/He and CO_2/He, and instrument calibration using KHP, sucrose, and the two calibration gases.

The end-of-run calibration consists of a set quantity of CH_4/He calibration gas which is automatically injected by the Carbon program. All FID readings during the analysis run are normalized to this peak to minimize the effects of FID performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis run and requires no operator intervention. The integrated calibration peak counts should be checked by the operator immediately after each run to insure that the analyzer is operating satisfactorily.

The manual calibration injections are performed at the beginning and ending of each analysis day, and serve to verify proper analyzer performance. The procedure for manual injections are described in Section 4.1 and 4.3.

Instrument calibration, performed twice a year or when a new calibration gas cylinder is started, establishes the calibration slope used in converting counts to μg of carbon, as explained in the next section. Instrument calibration involves spiking prefired quartz punches with various amounts of the 1800 ppm KHP and sucrose solutions (Section 3.1) and injecting various volumes of the CO_2 and CH_4 gases.

A clean blank quartz punch is baked in the analyzer oven at 800°C for 10 minutes using option 4 from the main menu of the carbon program. After the punch has cooled to less than 50°C, the KHP or sucrose solution (prepared as described in Section 3.1) is injected onto the punch using a 20 ml syringe. The following volumes are used:

- 5 ml KHP or sucrose solution
- 10 ml KHP or sucrose solution
- 15 ml KHP or sucrose solution (do twice)
- 20 ml KHP or sucrose solution
- no injection (as a system blank; see Section 4.2.2)
- 20 ml acidified DDW only (check of background level of DDW)

The sample port is sealed and the spiked filter punch is pushed to 1 cm from the sample oven. In this position the punch will experience a temperature of 35 to 40°C due to the heat from the oxidation oven. Allow the punch to dry thoroughly; the punch will turn from translucent to opaque as it dries. The punch must be dry to avoid water vapor effects on the FID. The OC/EC analysis option from the main menu is selected and started. The integrated peak counts for all seven temperature fractions for the sample peak and the calibration peak are recorded.

The CO_2 and CH_4 calibrations are run using the calibration options from the main menu. The following volumes are injected:

- 100 ml CO_2 or CH_4 gas (use 1000 ml syringe)
- 250 ml CO_2 or CH_4 gas (use 1000 ml syringe)
- 500 ml CO_2 or CH_4 gas (use 1000 ml syringe)
- 1000 ml CO_2 or CH_4 gas (do once with 1000 ml syringe and once with 2500 ml syringe)
- 2000 ml CO_2 or CH_4 gas (do with 2500 ml syringe)

Again, the integrated peak counts are extracted manually from the tabular printouts.

Calibration values are plotted as actual µg carbon vs. the ratio of the integrated sample peak counts to the calibration peak counts (Figure 3-1). Obvious outliers are identified and rerun. Linear regression is performed on each set of calibration data (separate calculations for KHP, sucrose, CH_4/He, and CO_2/He). The calibration slope derived from the CO_2 injections typically has a slightly different slope and does not fit as well. The slope (m) is calculated from:

$$\left(m = \frac{\sum (y_i \, x_i)}{\sum (x_i)} \right)$$

and the standard deviation (s) is calculated by:

$$\sigma = \sqrt{\frac{1}{n-1} \frac{\sum (y_i - m x_i)^2}{\sum x_i^2}}$$

where:

$$x_i = \frac{(\text{injected carbon peak area})}{(\text{calibration peak area})}$$

and:

$$y_i = \text{calculated carbon in spiked filter or manual injection } (\mu g)$$

Note that this is a special form of the regression formula, which insures that the curve passes through the origin.

The resulting slope is compared to previous calibration results. New values should be no more than ±10% different than previous calibrations if no major analyzer changes have been made.

The new slope for each analyzer (derived from combined CH_4, KHP, and sucrose data) is placed into the CARBON.DAT file for each analyzer; this file contains analyzer parameters

which are read into the Carbon program when it is first started. The date and version number in the CARBON.DAT file is also updated.

Calibration data and plots are retained in file folders in the file cabinet with raw analysis data.

5.2 Calculations

The conversion of integrated peak counts to μg of carbon for each peak in the thermogram is performed by the computer at the end of the analysis program. For reference purposes, the calculation is:

$$\text{peak } \mu\text{g C/punch} = \frac{(\text{Integrated peak counts above baseline})(\text{calibration slope})}{(\text{Internal calibration counts})}$$

The peaks reported are: four organic peaks (OC1, OC2, OC3, and OC4) corresponding to 120, 250, 450, and 550°C, respectively; three elemental carbon peaks (EC1, EC2, and EC3) corresponding to 550°C after the introduction of O_2, 700, and 800°C, respectively; and three pyrolyzed organic carbon peaks (Lower, Regular, and Upper Splits) corresponding to the peaks after the introduction of O_2 and before the Lower Split Time, Regular Split Time, and the Upper Split Time, respectively (see Section 1.7 and Figures 4-9 and 4-10).

Carbon values per punch are converted to μg C/cm^2 by:

$$\mu\text{g} \quad \text{C}/\text{cm}^2 = \frac{(\mu\text{g C/punch})}{(\text{punch area})}$$

Finally, carbon values are converted to μg C/filter by:

$$\mu\text{g C/filter} = (\mu\text{g C}/\text{cm}^2)\,(\text{filter deposit area})$$

6.0 QUALITY CONTROL

6.1 Performance Testing

System blanks are performed at the beginning of each week to insure the system is not introducing bias in the carbon results and to insure that the laser signal is not temperature dependent. Contamination is potentially due to:

- Operator practices, such as improper cleaning of tweezers and punch.
- Teflon particles on the push rod getting into the heated zone of the quartz oven.
- The sample boat contamination.
- The carrier gases contamination.

A temperature-dependent laser signal is potentially due to:

- Physical coupling of the push rod to the boat during the run.
- A quartz rod (laser light pipe) ready for replacement. Microscopic cracks in the quartz rod will increase internal reflectance of the laser light; as the number of these cracks multiply, the effect of temperature on these cracks, and thus on the reflectance, becomes an interference in the laser signal.

As described in Section 5.1, the calibration peak at the end of each analysis run serves as a regular standard; the integrated area under the calibration peak serves as a measure of analyzer performance. In addition, the daily injections of two calibration gases further serve as standards. Primary standards in the form of NIST-traceable spiked filter punches do not exist.

6.2 Reproducibility Testing

Replicates of analyzed samples are performed at the rate of one per group of ten samples. The replicate is selected randomly and run immediately after a group of ten is completed. The $\mu g/cm^2$ values for OC, EC, and TC are compared with the original run. The values should fall into the following criteria:

Range	Criteria
$< 10\ \mu g/cm^2$	$< \pm 1.0\ \mu g/cm^2$
$> 10\ \mu g/cm^2$	< 10 % of average of the 2 values

Notice that the criteria converge at 10 $\mu g/cm^2$. Replicates which do not fall within the above criteria must be investigated for analyzer or sample anomalies. Analyzer anomalies include poor response (as reflected in the calibration peak areas) or poor laser signals affecting the splits between OC and EC. Typical sample anomalies include inhomogeneous deposits or contamination during analysis. Inconsistent replicates for which a reason cannot be found must be rerun again.

6.3 Analysis Flags

During Level I validation (see Section 6.4), unusual conditions of the deposit or analysis problems are noted on the analysis printouts. Errors in pre-analysis data entry (e.g., in filter ID, punch area, deposit area) are corrected.

Flags are applied to the dBase file created from the analysis results ASCII file (see Section 6.4). The analysis flags commonly used are presented in Table 6-1. Note that all results flagged with "v" must include a description of the reason for invalidating the sample in the remarks field.

6.4 Data Validation and Feedback

6.4.1 Daily Validation

Level I validation is performed by manually checking the tabular and thermogram printouts the day after the analysis is performed. The laboratory supervisor or a designated technician is responsible for checking the data. The following items are checked on the tabular data (Figure 6-1):

- The filter ID is correct.
- For calibration injection runs, the carrier gas type is He/O_2 in the morning and He only in the afternoon, and the injection gas type is reversed between morning and afternoon injections.
- The analysis date is correct.
- The punch area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.
- The deposit area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.
- The calibration peak area is in the correct range (Section 4.1).
- The initial and final FID baseline are within 3 counts of each other; excessive FID baseline drift is cause for reanalyses. NOTE: Some very heavily loaded filters will have an FID baseline drift greater than 3 counts no matter which carbon analyzer the sample is run on, but typically a FID baseline drift greater than 3 counts signals either a problem with the run or with the carbon analyzer.

CARBON ANALYSIS RESULTS

Analyzer #4 Technician: KGG

Analysis ID : EL051Q-1.OEC
Sample ID : NEL051Q
Punch area : 0.536 cm2
Deposit area : 17.30 cm2

Analysis : 12/11/95 10:23 Calculation : 01/03/96 15:11

Anal program ver: P4.1 (11/21/95) Parm file ver : D4.04 (11/21/95)
Calib. slope : 22.25 ug C/peak ratio Baseline time : 90 sec
Calib. intercept: 0.00 ug C Baseline window : 1 counts
Reflectance unc.: 10 counts Transmission unc.: 10 counts
Sample transit : 28 sec Calib. transit : 45 sec

Calibration peak area: 23577 counts
Initial FID baseline : 205 counts
Final FID baseline : 206 counts

	Reflect Split Time	Laser	FID Split Time
Lower split :	1348 sec	1661 counts	1376 sec
Regular split:	1350 sec	1678 counts	1378 sec
Upper split :	1352 sec	1694 counts	1380 sec

	Peak Area		Carbon
OC Peak #1 :	356 counts	0.63 ug C/cm2	10.84 ug C/filter
OC Peak #2 :	1848 counts	3.25 ug C/cm2	56.29 ug C/filter
OC Peak #3 :	3681 counts	6.48 ug C/cm2	112.12 ug C/filter
OC Peak #4 :	2390 counts	4.21 ug C/cm2	72.80 ug C/filter
Lower pyro'd OC :	533 counts	0.94 ug C/cm2	16.23 ug C/filter
Reg. pyro'd OC :	602 counts	1.06 ug C/cm2	18.34 ug C/filter
Upper pyro'd OC :	673 counts	1.18 ug C/cm2	20.50 ug C/filter
EC Peak #1 :	3310 counts	5.83 ug C/cm2	100.82 ug C/filter
EC Peak #2 :	265 counts	0.47 ug C/cm2	8.07 ug C/filter
EC Peak #3 :	58 counts	0.10 ug C/cm2	1.77 ug C/filter

****

	VOC	Regular OC	High Temp OC	Regular EC	High Temp EC	TC	
Lower split :	0.6	15.5	14.9	5.5	0.6	21.0	ug C/cm2
	10.8	268.3	257.4	94.4	9.8	362.7	ug C/filter
Regular split:	0.6	15.6	15.0	5.3	0.6	21.0	ug C/cm2
	10.8	270.4	259.5	92.3	9.8	362.7	ug C/filter
Upper split :	0.6	15.8	15.1	5.2	0.6	21.0	ug C/cm2
	10.8	272.6	261.7	90.2	9.8	362.7	ug C/filter

****

OC/TC: 0.75
EC/TC: 0.25
OC/EC: 2.93

Figure 6-1. Example Level I Validated Tabular Printout.

Table 6-1

Common DRI Analysis Flags

Flag	Description
b1	Field blank
b2	Lab blank
b6	Transport blank
f1	Filter damaged outside of analysis area
f2	Filter damaged inside analysis area
i2	Inhomogeneous filter deposit - random areas of darker or lighter deposit
g4	Deposit falling off (usually occurs on heavily loaded samples)
i4	Abnormal deposit area, possible air leakage during sampling
m2	Non-white sample punch after analysis
r1	Replicate on same analyzer
r5	Replicate on different analyzer
v	Sample void

- The lower laser split time and the upper laser split time are within 10 seconds of each other. If the times differ by more than 10 seconds, check that the lower split OC and upper split OC differ by no more than 5%. OC values which differ by more than 5%, unless due to a small change in laser signal resulting from an extremely clean or very dark sample, requires reanalysis.

- Calculated carbon values for calibration injection runs are within 10% of the current mean value for the injected gas type on that analyzer.

- Acceptance runs for prefired quartz filters result in < 1.5 $\mu g/cm^2$ OC, < 0.5 $\mu g/cm^2$ EC, and < 2.0 $\mu g/cm^2$ TC. Filters which exceed these levels must be refired.

Items which are found to be okay are underlined in red. Items which have problems are circled in red.

The thermograms are checked for the following (Figure 6-2):

- The initial FID baseline is flat, indicating that the analyzer has been thoroughly purged before analysis began.

- The final FID baseline prior to the calibration peak is within 3 counts of the calculated FID baseline; excessive drift is cause for reanalysis.

- The laser signal during the first 90 seconds appears near the bottom of the graph (no reflectance); an excessively high initial laser is an indication that the internal reflectance of the quartz rod is too high, either due to too many internal cracks or a complete fracture of the rod. High initial laser signals should result in a physical inspection of the analyzer.

- The initial laser line drawn on the thermogram matches the laser signal immediately after the rod is pushed in. A laser line which is too low is an indication that the sample was not pushed into the oven in time; a laser signal which exceeds the calculated initial laser signal is a symptom of physical coupling between the sample boat and the push rod, although some automobile emission samples also show this characteristic; a spike or a number of jumps in the laser signal indicates that the operator had difficulty in decoupling the boat from the push rod. All of these problems are grounds for reanalysis if severe.

- The laser signal should dip below the initial laser line until oxygen is introduced at 550°C, at which the signal should rise steeply.

- The laser signal at the end of the analysis is flat; if the laser signal dips as the oven begins to cool, the boat is physically coupled to the push rod and the laser signal during the rest of the analysis is suspect.

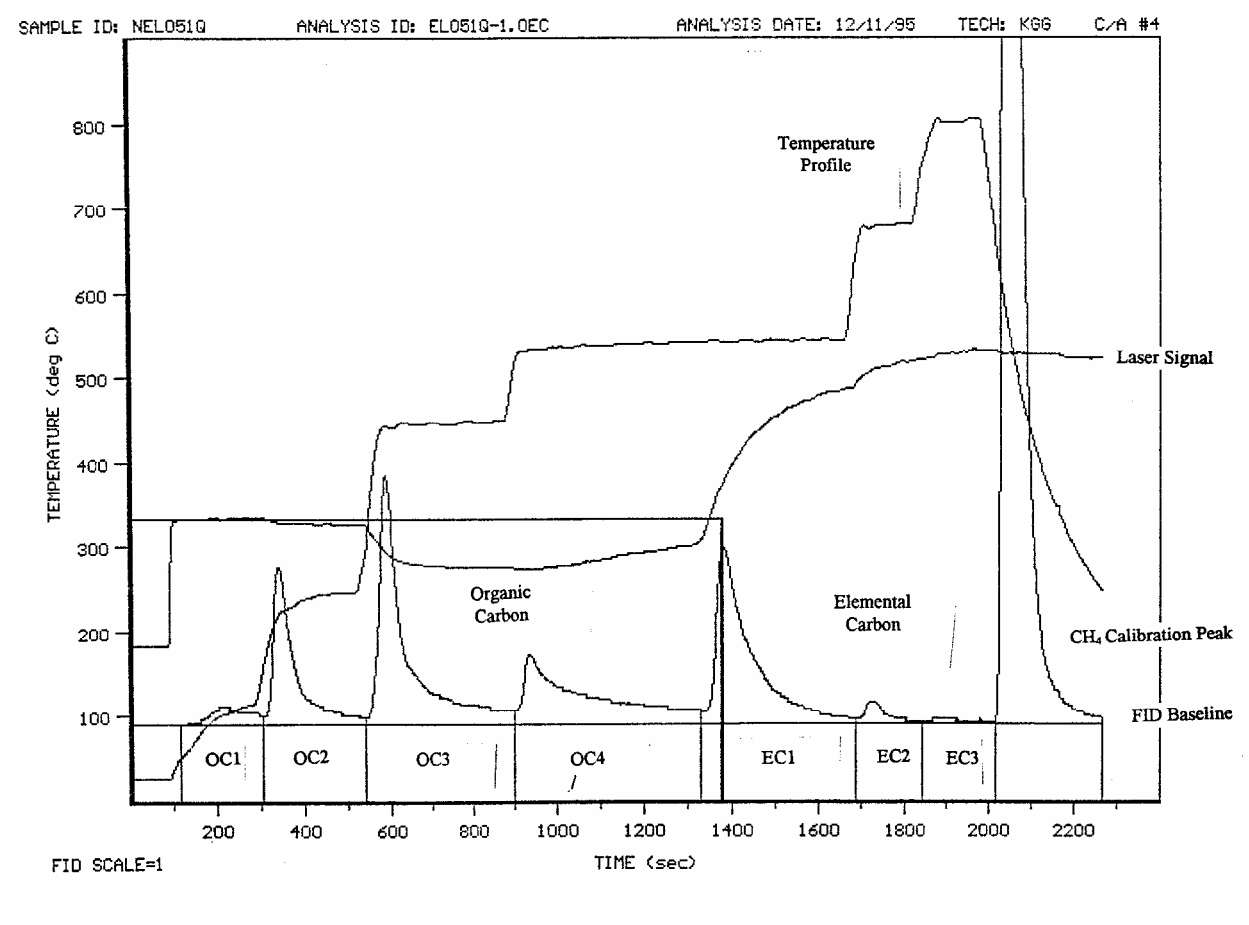


Figure 6-2. Example Level I Validated Thermogram Printout.

- The temperature readings reflect stable and smooth temperatures at each level and quick transitions between levels.

Problems or deviations from normal should be circled in red. If the sample punch taped to the thermogram is not white, it is also circled.

If examination of the tabular and thermogram printouts result in a decision that a sample should be reanalyzed, write "Rerun" in red on the printouts and prepare a reanalysis list. This list should be posted immediately after the validation is complete, and those samples should be rerun as soon as they can be conveniently fit into the current day's analyses.

Evidence of persistent analyzer problems must be resolved, either by physically examining the analyzer or reviewing the problems with the analyzer operator.

6.4.2 Validation of Final Data File

The following steps are followed to create a dBase file containing carbon data and to perform Level "I" validation on it:

- Obtain copies of the latest version of the summary file from the directory corresponding to the desired project. These files are called **CPEAKS.n**, where n is the carbon analyzer number. These files may be either copied from the backup files or copied directly from the carbon analyzer computers. The latter method is recommended, as it guarantees that the summary files retrieved are the latest versions. These files are updated at the end of each analytical run, so the latest version is necessary to insure that all of the analyses are included.

- Copy the files to the working directory:

  The ASCII **CPEAKS.n** file is reformatted, sorted, and placed into a dBase III file by the following:

  INPCARBN <Return>

  The **INPCARBN** program will prompt the user for an output file name. The dBASE file naming convention calls for a name in the following format:

  xxOETnnt.DBF

  where:

  xx is the 2 character project identifier

  OET stands for organic/elemental carbon

nn is the 2 digit batch number (generally used to distinguish between different projects for the same client or between sampling quarters for an extended project)

t stands for the sample type based on sampler technology:

A	Agricultural burn emissions dilution sampler
C	Combination particle/gaseous sampler
D	Dichot (both $PM_{2.5}$ and PM_{10})
G	Gaseous
H	High-volume sampler
I	IMPROVE/NPS sampler
P	Portable Survey Sampler
Q	Audit samples
R	Resuspension chamber
S	Sequential filter sampler (SFS)
W	Wet Deposition
X	Unknown
Y	Y-sampler (DRI source sampler)

The final dBase file name is specified in the analysis list posted in the carbon room.

After the **INPCARBN** program produces the dBase output file, the program will alert the operator that it is ready to print the contents of that file. Although the **INPCARBN** program is capable of printing the carbon data file, it is recommended that *Microsoft Excel* be used to print the file. If the file is opened in *Excel*, the uncertainty columns deleted, and the page setup set to landscape mode and fit to one page wide by many pages long, a good printout will be produced on a laserjet printer. If you must use the INPCARBN program to print the carbon data file, a wide carriage dot matrix printer is recommended.

After the printout is produced, immediately label the top of the printout with the file name and printout date. This can also be accomplished by using a labeling header in *Excel*.

Begin validation by matching the filters listed on the analysis list with the filters listed on the dBase printout. There must be at least one entry on the printout for every filter listed on the analysis list.

Flag field and lab blanks as the list is reviewed by placing "b1", "b2", or "b6" in the second column of the printout. Because the dBase printout is sorted by ID number, replicates and reruns will be grouped together.

Indicate missing data by writing the missing filter ID in the margin with an arrow drawn to the appropriate place of insertion. Scan the printout for unusual IDs which may have been mistyped during analysis. Generally these will appear at the beginning or end of the printout due to the sorting process. Make sure that all samples listed on a rerun list appear on the printout.

Resolve all missing data. If a large amount of data is missing because of analysis in the incorrect subdirectory, it is generally easier to retrieve the summary file from that incorrect subdirectory, trim the unnecessary data from that file using a word

processor, combine the remaining data with the **CPEAKS.n** file, and rerun the **INPCARBN** program. If only a few data points are missing, it is generally not too much trouble to simply write the correct values from the daily folders on the printout and add those values manually to the dBase files at the same time the flags and other corrections are made.

Scan the deposit area column for incorrect entries. Circle the incorrect entries to insure that corrected values replace those currently in the database.

Scan the filter IDs for multiple entries of ID numbers. Under normal conditions, the only times multiple entries should occur are reruns and replicates. All multiple entries must be flagged to indicate the reason for their existence.

Scan for missing runs. The most common example is the first run being aborted or lost for some reason, and the only entry in the dBase file is the second run. An entry for the first run must be inserted, flagged as invalid, and labeled as to the reason it was invalid. All punches taken from the filters MUST be accounted for.

Scan the OC and EC columns looking for unusually high or low values. At this time make sure that the field blanks and/or lab blanks are all close to one another. Circle any possible outliers for further investigation.

Finally, pull the analysis folders and go through the analysis summaries and thermograms one by one. At this time, resolve all circled items and all missing flags. Determine if analyses flagged by the operator are legitimate. These flags are determined by the operator at the end of the analysis run (Section 4.2 and Figure 4-11); these flags are defined in Table 6-2. If the temporary flag is not warranted, draw a line through the flag to indicate it should be removed. If the sample should be rerun, add it to a rerun list. If the analysis has some anomaly but still appears to be legitimate, either flag or add notes to the comments field as appropriate. Analysis flags are defined in Section 6.3. All samples flagged as invalid must have an entry in the comments field to describe the reason that the sample is invalid. Common notes and comments are presented in Table 6-3.

All operator-generated flags must be either converted to standard analysis flags or removed. The flags in Table 6-2 are temporary flags only and are not recognized as legitimate analysis flags at DRI.

After all thermograms have been reviewed and all possible reruns have been identified, post the rerun list in the carbon room and have the reruns done as soon as possible.

Review the data from the reruns, looking for inconsistencies. Insure that the reasons for the rerun have been addressed. Mark the printout with the new values for manual insertion into the dBase file. Previous runs must be flagged as invalid or the reruns flagged as replicates.

Finally, all comments, flags, insertions, and other changes made to the printout are entered into the dBase file. After all changes are made, generate a new printout. Label the new printout with the file name and printout date. Forward a copy of the printout and the dBase file on disk to the person putting the final report together.

6.4.3 Use of the CARBVAL Program to Assist in Data Validation

A *Microsoft FoxPro* program named CARBVAL exists which will greatly assist in the validation process. When you use the CARBVAL program, you must specify if you are validating a data file which contains IMPROVE data or not. There are several validation steps that the CARBVAL program performs which are specific to IMPROVE.

The CARBVAL program will perform the following validations:

1. Identify records where the deposit area (deparea) is not equal to the deposit area entered by the user.

2. Identify records with duplicate runids.

3. Identify records before/after which contain gaps in runid sequence

4. Identify filters with more than one original run.

5. Identify records where elemental carbon concentration is greater than organic carbon concentration.

6. Identify blank filters where organic carbon concentration is greater than 3.95*deparea

7. Identify blank filters where elemental carbon concentration is greater than deparea

8. Identify records where organic carbon concentration divided by the total carbon conentration is less than specified value (default is 0.75).

9. Identify voided samples that do not have a value in the comments column.

10. Identify replicate records incorrectly classified as ‘r1’ or ‘r5’.

11. Identify samples where a ‘m2’ flag was not present in both the original and replicate runs.

12. Identify replicate runs where ‘octc’, ‘ectc’, or ‘tctc’ values are not within 10% or the deparea (in µg/filter) of original run.

13. IMPROVE only: Identify records where filter channel value is not equal to ‘C’.

14. IMPROVE only: Identify records where filter type is not primary or secondary.

15. IMPROVE only: Identify secondary filters where ‘ectc’ value > 3.8 or ‘octc’ > 18.

16. IMPROVE only: Identify secondary filters where ‘ectc’ or ‘octc’ values are > corresponding primary filter values.

17. IMPROVE only: Identify records where ‘samdate’ or ‘week’ values are empty.

18. IMPROVE only: Identify records with incorrect values in the ‘day’ field.

To use the CARBVAL program, first start *Microsoft FoxPro*. Then type ‘DO CARBVAL’ from the command window. The program will start and ask you for a file name. The program will then ask you a series of questions:

• the name of file used to store validation results,

• the deposit area of filter in square centimeters,

• the expected number of filters,

• and the octc/tctc ratio threshold (default = 0.75).

After the above values are entered, the CARBVAL program will begin validating the selected file. If the preliminary checks are satisfactory, the program will also ask you if you want to remove the carbon technicians validation flags and if you want to replace the ‘r’ replicate flag with the appropriate ‘r1’ or ‘r5’ validation flag. When the program is finished, it will allow you to browse the problem records on screen and will also print them.

It is recommended that you run the CARBVAL program as a first check after you have put the carbon data file together and then run it again as necessary, but certainly run it again when the final database is assembled. This will serve as a final check on the database.

Table 6-2

DRI Carbon Analysis Temporary Flags

Flag	Description
EI	Error in sample ID
EA	Error in sample deposit area
ST	Suspect temperature profile
SF	Suspect FID signal
SL	Suspect laser signal
Mi	Miscellaneous problem
v	Invalid run
r	replicate
b	blank
i	inhomogeneous filter deposit
f	filter media damaged
g	sample deposit damaged
d	sample dropped
n	foreign substance on filter deposit
w	sample wet

Table 6-3

DRI Carbon Analysis Validation Comments

Comments	Description
"Anomalous laser"	Despite good initial laser, laser signal drifted above initial laser signal before dropping (typical of auto emissions)
"Operator error"	Used with "v" flag; operator missed pushing boat in, pushed abort key, pushed manual advance key at an inappropriate time, etc.
"Analyzer malfunction"	Used with "v" flag; analyzer malfunction or problem beyond the control of the operator such as plugged FID, broken oven heater, etc.
"Poor replicate"	Replicate is outside the normal criteria, but no reason can be found for the discrepancy.
"Poor initial laser"	Used with "v" flag; severe coupling or boat not pushed in time for calculation of initial laser signal.
"Sample contaminated"	Used with "v" flag; rerun of sample yields lower values or different peaks. Typically used with blanks or reruns of replicates.
“Temperature problem”	Used with “v” flag, one or more of the temperature steps were not properly obtained. The most common example is the over-shooting of the first (120°C) temperature step.

7.0 REFERENCES

Fung, K. (1986). Environmental Research and Technology, Inc., Newbury Park, CA. Personal Communication.

Huntzicker, J.J. (1986). Oregon Graduate Center, Beaverton, OR. Personal Communication.

Johnson, R.L., J.J. Shah, R.A. Cary, and J.J. Huntzicker (1981). "An Automated Thermal-Optical Method for the Analysis of Carbonaceous Aerosol." In *Atmospheric Aerosol, Source/Air Quality Relationships*, E.S. Macias and P.K., Hopke, eds. ACS Symposium Series, No. 169. American Chemical Society, Plenum Press, New York, NY.

Lin, C. and S.K. Friedlander (1988). "A Note on the Use of Glass Fiber Filters in the Thermal Analysis of Carbon Containing Aerosols." Technical Note, *Atmospheric Environment*, 3, 605-607.

Rau, J.A. (1986). "Residential Wood Combustion Aerosol Characterization as a Function of Size and Source Apportionment Using Chemical Mass Balance Modeling." Thesis, Oregon Graduate Center.

APPENDIX A.6

DRI STANDARD OPERATING PROCEDURE — Pages: 16

Title: Extraction of Ionic Species From Filter Samples — Number: 2-109.5 — Revision: 5

1.0 GENERAL DISCUSSIONS

1.1 Purpose of Procedure

This method describes the procedures to extract ions from Teflon, quartz, and nylon filters and from impregnated triethanolamine (TEA), citric acid (CA), and potassium carbonate (K_2CO_3) filter samples. These filters are used in the various ambient and source monitoring programs at DRI.

1.2 Measurement Principle

(Not applicable.)

1.3 Measurement Interferences and their Minimization

Prepare one method (reagent) blank for every 40 extracted filter samples by filling an empty extraction vial with the same type and amount of extraction solution used to extract the samples. Run the method blank by sonication or shaking to check for background contamination from the extraction vials or from the extraction process.

1.4 Ranges and Typical Values of Measurements

(Not applicable.)

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

(Not applicable.)

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure (SOP) prior to performing filter extraction, which includes solution preparation and filter extraction.

The laboratory manager or supervisor must ensure that the extraction procedures are properly followed, maintain the supplies necessary to ensure uninterrupted extraction, and oversee proper chain-of-custody documentation.

The quality assurance (QA) officer of DRI's Environmental Analysis Facility (EAF) determines the extent and methods of QA to be applied to each project, estimates the level of effort involved in this quality assurance, and ensures that these tasks are budgeted and carried out as part of the performance on each contract. The QA officer is responsible for updating this procedure periodically.

1.7 Definitions

(Not applicable.)

1.8 Related Standard Operating Procedures (SOPs)

2-104.2 Impregnating, Drying, and Acceptance Testing of Filters for Sampling Gas in Air

2-108.4 Sectioning of Filter Samples

2-203.4 Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography

2-207.2 Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetry

2-206.2 Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy

2-208.1 Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography

2.0 APPARATUS INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Supplies

2.1.1 Filter Media

- Teflon-membrane filters, Teflon 2 μm pore size, 47 mm (#R2PJ047); Teflon 2 μm pore size, 37 mm^2 μm pore size, (#R2PJ037); or Zeflour 2 μm, 47 mm (#P5TJ047) (Pall Sciences, Ann Arbor, MI).

- Quartz fiber filters: 25 mm, 37 mm, or 47 mm, Pall 2500 QAT-UP quartz-fiber filters (Pall Sciences, Ann Arbor, MI).

- Nylasorb filters, 1.0 micron, 47 mm (Pall Sciences, Ann Arbor, MI).

- K_2CO_3 -impregnated, 47 mm, Whatman 31ET cellulose fiber filters (Chemtrex, Hillsboro, OR).

- Citric Acid-impregnated, 47 mm, Whatman 31ET cellulose fiber filters (Chemtrex, Hillsboro, OR).

- TEA-impregnated, 47 mm, Whatman 31ET chromatography filter (Chemtrex, Hillsboro, OR).

2.1.2 Additional Supplies

- Flat-tipped Tweezers (Millipore, San Francisco, CA)
- Gloves, non-powdered, no particular manufacturer
- Repipet II –10 ml and 20 ml
- Polystyrene, 15 ml conical extraction tubes, 17 mm x 120 mm.
- Eppendorf Pipet, 200 µl
- Sonicator, Branson Model 5200 (Cole Parmer, Vernon Hills, IL)
- Shaker Model 51401-00 (Cole Parmer, Vernon Hills, IL)
- Class A volumetric flasks, 500 ml and 1000 ml
- Class A 5 ml graduated pipet
- Weighing boats, disposable polystyrene
- Glass extraction tubes (30 ml) with screw caps

2.2 Reagents

2.2.1 Grade and Purity.
All chemicals used to prepare extraction solution should be of American Chemical Society (ACS) reagent-grade purity. Dry all anhydrous chemicals at 105 °C for 1–2 hours, then cool in a desiccator before weighing. Warning: Do not dry hydrated salts in oven.

- Sodium carbonate, anhydrous (Na_2CO_3)
- Sodium bicarbonate ($NaHCO_3$)
- Hydrogen peroxide (H_2O_2), 30%
- Sodium citrate dihydrate ($Na_3C_6H_5O_7\ 2H_2O$)
- Cesium chloride (CsCl)
- Lanthanum Nitrate, hexahydrate ($La(NO_3)_3\ 6H_2O$)
- Nitric Acid, 70-71 percent (HNO_3), trace metal grade
- Distilled-deionized water (DDW) with a resistance of 18 megaohms or less. DRI uses a Millipore water purification system (Milli-Q™) to achieve a

required specification conforming to ASTM D1193, Type II (Annual Book of ASTM Standard, 1983).

2.2.2 Solutions

- Sodium carbonate (0.1M): Weigh 10.60 g. Na_2CO_3 (to the nearest 0.01 g.) into a disposable weighing boat. Transfer the chemical quantitatively to a 1000 ml volumetric flask by rinsing it into the flask with DDW from a wash bottle. Dilute to the 1000 ml mark with DDW.
- Sodium bicarbonate (0.1M): Weigh 8.40 g. $NaHCO_3$ (to the nearest 0.01 g) into a disposable weighing boat. Transfer the chemical quantitatively to a 1000 ml volumetric flask by rinsing it into the flask with DDW from a wash bottle. Dilute to the 1000 ml mark with DDW.
- Sodium carbonate/bicarbonate (0.0035 M/0.0017 M) combined eluent: Using a grade A graduated cylinder, measure 140 ml 0.1M Na_2CO_3 into a 10 L carboy. Using the same graduated cylinder, measure 68 ml 0.1M $NaHCO_3$ into the same carboy container. Dilute to 4 L; mix well.
- Sodium carbonate/bicarbonate (0.0018 M/0.0017 M) combined eluent (for analysis of chloride on nylon filters): Using a grade A graduated cylinder, measure 72 ml 0.1M Na_2CO_3 into a 10 L carboy. Measure 68 ml 0.1 M $NaHCO_3$ into the carboy. Dilute to 4 L, mix well.
- Sodium citrate dihydrate (0.1 M): Weigh 29.00 g. $Na_3C_6H_5O_72H_2O$ (to the nearest 0.01 g) into a disposable weighing boat. Transfer the chemical quantitatively to a 1000 ml volumetric flask by rinsing it into the flask with DDW from a wash bottle. Dilute to the mark with DDW.
- Hydrogen peroxide, 0.1% solution: Using a 5 ml graduated pipette, measure 3.33 ml of 30% H_2O_2 into a 1000 ml. volumetric flask. Dilute to the mark with DDW.
- Nitric acid (2.6 M): Using a 100 ml graduated cylinder, measure 167 ml concentrated nitric acid (trace metal grade only) into a 1000 ml volumetric flask containing 600 ml of DDW. Swirl gently. Dilute to the mark with DDW; mix gently and thoroughly.

2.3 Forms

- DRI Filter Extraction Data Log Sheet (Table 2-1)
- DRI SO_2 Extract Dilution Data Log Sheet (Table 2-2)

3.0 CALIBRATION STANDARDS

(Not applicable.)

DRI Filter Extraction Log Sheet

Extraction Date	Project	Filter Size (mm)	Area Used	Solution Type (conc.)	Sonication				Shaking			Comments
					Start Time	Start Temp (°C)	Stop Time	Stop Temp (°C)	Start Time	Stop Time	Tech.	

Table 2-1.

DRI SO_2 Extract Dilution Data Log Sheet

Project	Inclusion Label ID	Extraction Date	Extract Volume (ml)	Extract Solution Type (conc.)	Dilution Date	Dilution Volume (ml)	Dilution Solution Type	Sonication				Tech Init	Comments
								Start Time	Start Temp (°C)	End Time	End Temp (°C)		

Table 2-2.

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram for this procedure is shown in Figure 4-1.

4.2 Extraction of Teflon Filters

4.2.1 The following procedure is used for extracting the filters for analyses of chloride (Cl^-), nitrate (NO_2^-) and sulfate ($SO_4^=$) by ion chromatography (IC); ammonium (NH_4^+) by automated colorimetry (AC); and cations (Na^+, K^+, Ca^{++}, Mg^{++}) by atomic absorption spectroscopy (AAS) or IC. Before extracting Teflon filters, confirm that final weights have been obtained and recorded for all the filters being extracted, including any pertinent laboratory blanks.

- Depending upon the analysis list instructions, place either whole filters or half filters into 15 ml sterile polystyrene tubes having twist seal caps when they are removed from their storage PetriSlides. (See 2-108.4, Sectioning of Filter Samples.) Extract, sonicate, and shake the samples in batches of 40 or less. Label the extraction tubes with barcode labels that identify the samples. (Caution: Verify the barcode label against the DRI chemical analysis list.)
- Calibrate the Repipet II filled with DDW to 15.0 ml by positioning the adjustable meniscus to 15 ml, pipetting the solution into a tared weighing boat, and weighing on the Mettler AE200 balance. Adjust meniscus as necessary to achieve 15.00 g.(to the nearest 0.01g.)
- Using an Eppendorf pipet, add 200 µl ethanol onto Teflon filter surface as a wetting solution. Make sure the ethanol directly contacts the Teflon filter surface. Shake the tube, if necessary, to wet the filter.
- Add 10.0 ml DDW to each filter sample in the extraction tube using the Repipet II. Note: When samples are ready to extract, pour out any residual water in the repipet and use fresh DDW from the polisher.
- Place 200 µl ethanol in an empty extraction tube, add 10.0 ml DDW and mark the tube as a method blank. Each prepared tray of extracted samples must have one method blank.
- Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.
- Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level.
- Measure the temperature. If the bath temperature is above 20 °C, add ice until it reaches at least 18.5°C. Record the temperature on the Extraction Data Log Sheet.
- Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at 30 minutes and at 60 minutes. If the temperature exceeds 25 ºC, add ice to bring the temperature

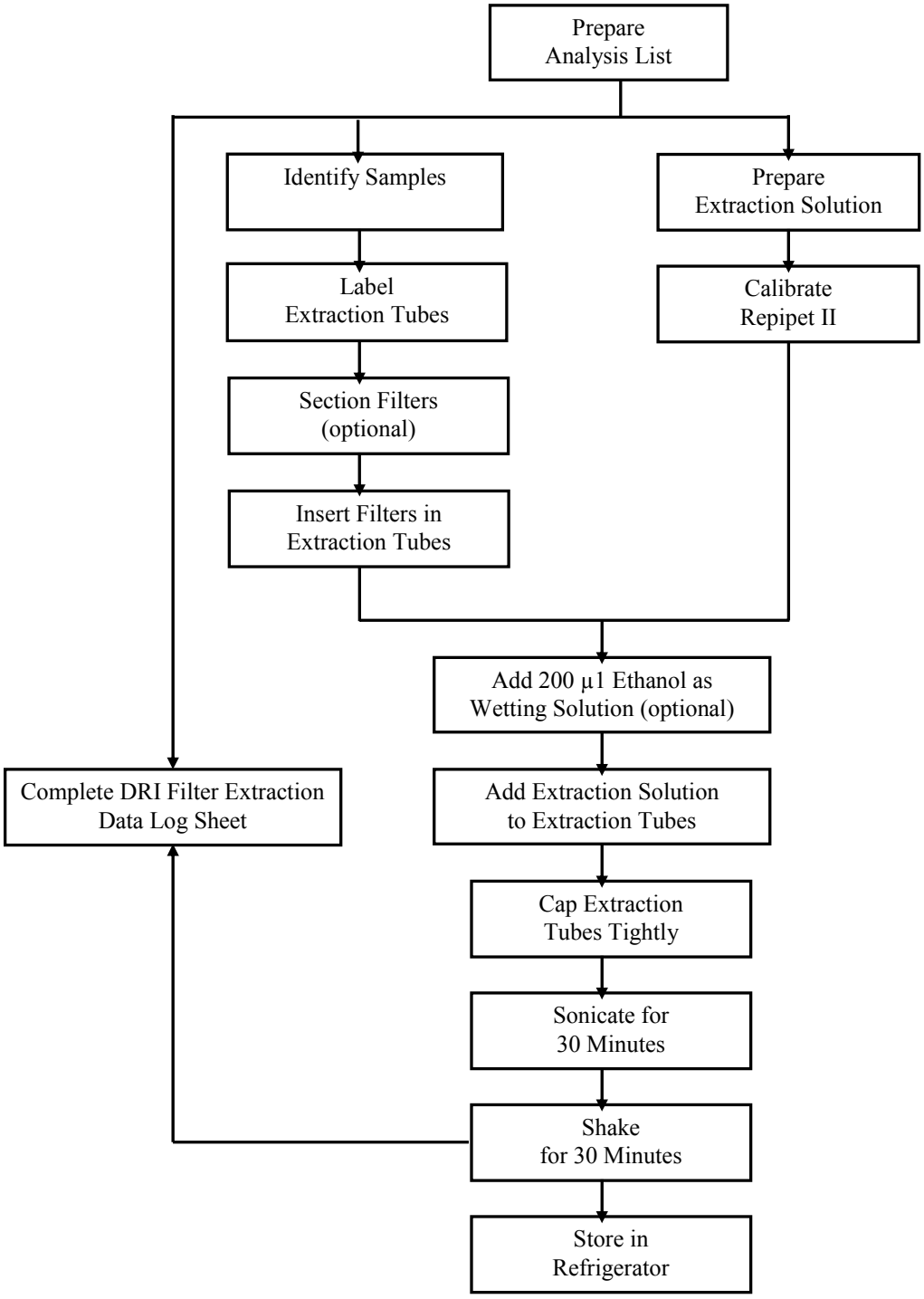

Prepare
Analysis List
Identify Samples
Prepare
Extraction Solution
Label
Extraction Tubes
Calibrate
Repipet II
Section Filters
(optional)
Insert Filters in
Extraction Tubes
Add 200 µ1 Ethanol as
Wetting Solution (optional)
Complete DRI Filter Extraction
Data Log Sheet
Add Extraction Solution
to Extraction Tubes
Cap Extraction
Tubes Tightly
Sonicate for
30 Minutes
Shake
for 30 Minutes
Store in
Refrigerator

Figure 4-1. Flow diagram for extraction process.

down. (Caution: Keep the water in the bath at or below ambient temperature during the extraction.). Record the temperature on the Extraction Data Log Sheet.

- Install the extraction rack on the shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).
- Fill out the DRI Filter Extraction Data Log Sheet (Table 2-1).
- Store the extracted samples overnight in the refrigerator prior to chemical analysis.

4.3 Extraction of Triethanolamine (TEA)-Impregnated Whatman 31ET Chromatography Filters

4.3.1 Follow this procedure to extract impregnated filters and for the analysis of NO_2^- by Technicon AC, and analysis of NO_2^- and nitrate (NO_3^-) by IC.

- Depending upon analysis list instructions, remove either whole filters or half filters from their storage PetriSlides and place them in 15 ml sterile polystyrene tubes that have twist seal caps. (See 2-108.4, Sectioning of Filter Samples.) Extract, sonicate, and shake the samples in batches of 40 or less. Label the extraction tubes with barcode labels. (Caution: Verify the barcode label against the DRI chemical analysis list.)
- Calibrate the Repipet II filled with DDW to 10.0 ml (Section 4.2.4).
- Add 10.0 ml DDW to each filter sample in the extraction tube using the Repipet II.
- Add 10.0 ml of DDW to one empty extraction tube, and mark the tube as reagent blank.
- Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.
- Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level.
- Measure the temperature. If the bath temperature is above 20 °C, add ice until it reaches at least 18.5°C. Record the temperature on the Extraction Data Log Sheet.
- Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at 30 minutes and at 60 minutes. If the temperature exceeds 25 ºC, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (Caution: The water in the bath should be kept at or below ambient temperature during the extraction.) Record the temperature on the Extraction Data Log Sheet.
- Install the extraction rack on the shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3). Fill out the DRI Filter Extraction Data Log Sheet (Table 2-1).
- Store the extracted samples in the refrigerator prior to chemical analysis. Complete the entries on the DRI Filter Extraction Data Log Sheet (Table 2-1).

4.4 Extraction of Nylon Filters

4.4.1 Follow this procedure to extract filters for the analyses of NO_3^- and $SO_4^=$ by IC.

- Depending upon analysis list instructions, remove either whole filters or half filters from their storage PetriSlides and place them in 15 ml sterile polystyrene tubes that have twist seal caps. (See 2-108.4, Sectioning of Filter Samples.) Extract, sonicate, and shake the samples in batches of 40 or less. Label the extraction tubes with barcode labels that identify the samples. (Caution: Verify the barcode label against the DRI chemical analysis list.)
- Calibrate the Repipet II filled with sodium carbonate/bicarbonate eluent to 10.0 ml. (See section 4.2.4.)
- Add 10.0 ml of appropriate sodium carbonate/bicarbonate eluent (see Section 2.2.2) to each filter sample in the extraction tube using the Repipet II.
- Add 10.0 ml extraction solution to an empty extraction tube and label the tube as a method blank.
- Cap the tubes tightly. Be sure that the exposed area on the filter remains completely immersed in the extraction solution.
- Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level.
- Measure the temperature. If the bath temperature is above 20 °C, add ice until it reaches at least 18.5°C. Record the temperature on the Extraction Data Log Sheet.
- Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at 30 minutes and at 60 minutes. If the temperature exceeds 25 ºC, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (Caution: The water in the bath should be kept at or below ambient temperature during the extraction.) Record the temperature on the Extraction Data Log Sheet.
- Install the extraction rack on the shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3). Fill out the DRI Filter Extraction Data Log Sheet (Table 2-1).
- Store the extracted samples in the refrigerator prior to chemical analysis. Complete the entries on the DRI Filter Extraction Data Log Sheet (Table 2-1).

4.5 Extraction of Quartz Filters

4.5.1 Follow this procedure to extract for analyses of Cl^-, NO_3^-, $SO_4^=$ by IC, NH_4^+ by AC, and Na^+ or K^+ by AAS.

- Depending upon analysis list instructions, remove either whole filters or half filters from their storage PetriSlides and place them in 15 ml sterile polystyrene tubes that have twist seal caps. (See 2-108.4, Sectioning of Filter Samples.) Extract, sonicate, and shake the samples in batches of 40 or less.

Label the extraction tubes with barcode labels that identify the samples. (Caution: Verify the barcode label against the DRI chemical analysis list.)

- Refer to Section 4.2.4 for calibration of Repipet II.
- Add 15.0 ml DDW to each filter sample in the extraction tube using the Repipet II.
- Add 15.0ml of DDW to one empty extraction tube. Mark this tube as reagent blank.
- Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.
- Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level.
- Measure the temperature. If the bath temperature is above 20 °C, add ice until it reaches at least 18.5°C. Record the temperature on the Extraction Data Log Sheet.
- Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at 30 minutes and at 60 minutes. If the temperature exceeds 25 ºC, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (Caution: The water in the bath should be kept at or below ambient temperature during the extraction.) Record the temperature on the Extraction Data Log Sheet.
- Install the extraction rack on the shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3). Fill out the DRI Filter Extraction Data Log Sheet (Table 2-1).
- Store the extracted samples in the refrigerator prior to chemical analysis. Complete the entries on the DRI Filter Extraction Data Log Sheet (Table 2-1).

4.7 Extraction of K_2CO_3-Impregnated Whatman 41 Cellulose Filters or K_2CO_3-Impregnated Pallflex 2500 QAT-UP Quartz Fiber Filters.

4.7.1 Follow this procedure to extract K_2CO_3 impregnated filters for the analyses of sulfur dioxide (SO_2) and $SO_4^=$ by IC.

- Depending upon analysis list instructions, remove either whole filters or half filters from their storage PetriSlides and place them in 15 ml sterile polystyrene tubes that have twist seal caps. (See 2-108.4, Sectioning of Filter Samples.) Extract, sonicate, and shake the samples in batches of 40 or less. Label the extraction tubes with barcode labels that identify the samples. (Caution: Verify the barcode label against the DRI chemical analysis list.)
- Calibrate the Repipet II filled with 0.1% H_2O_2 extraction solution to 10.0 ml (See Section 4.2.5).
- Add 10.0 ml extraction solution to each extraction tube using a Repipet II.

- Add 10.0 ml extraction solution to one empty extraction tube and mark the empty tube as a method blank. Prepare one blank per rack (40 or less) of samples.
- Cap the tubes tightly. Be sure that the exposed area on the filter remains completely immersed in the extraction solution.
- Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level.
- Measure the temperature. If the bath temperature is above 20 °C, add ice until it reaches at least 18.5°C. Record the temperature on the Extraction Data Log Sheet.
- Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at 30 minutes and at 60 minutes. If the temperature exceeds 25 ºC, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (Caution: The water in the bath should be kept at or below ambient temperature during the extraction.) Record the temperature on the Extraction Data Log Sheet.
- Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1) and complete the required information on the DRI SO_2 Extract Dilution Data Log Sheet (Table 2-2).
- Install the extraction rack on the shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).
- Store the extraction tubes in the refrigerator for two days. (Caution: Store the samples in 0.1% H_2O_2 solution for two days to ensure that all SO_2 and $SO_3^=$ are oxidized to $SO_4^=$.)
- Fill in all entries on the DRI SO_2 Extract Dilution Data Log Sheet (Table 2-2).
- Calibrate a Repipet II filled with DDW to 10.0 ml. (Section 4.2.5).
- Prepare a new set of extraction vials. Make sure the label IDs match those on the previous extraction vials (from two days previously.)
- Pipet 1.0 ml of each extract into its corresponding empty extraction tube. Using the calibrated Repipet II, add 10.0 ml DDW to each tube.
- Store the extracted samples in the refrigerator overnight prior to chemical analysis.

4.8 Extraction of Citric Acid-Impregnated Whatman 41 Cellulose Fiber Filters.

4.8.1 Follow this procedure to extract impregnated filters and for the analysis of NH_4^+ by Technicon AC or by IC.

- Depending upon analysis list instructions, remove either whole filters or half filters from their storage PetriSlides and place them in 15 ml sterile polystyrene tubes that have twist seal caps. (See 2-108.4, Sectioning of Filter Samples.) Extract, sonicate, and shake the samples in batches of 40 or less. Label the extraction tubes with barcode labels that identify the samples. (Caution: Verify the barcode label against the DRI chemical analysis list.)

- For IC: Calibrate the Repipet II filled with DDW to 10.0 ml by weighing. For AC: Calibrate the Repipet II filled with 0.1 M sodium citrate to 10.0 ml by weighing. This buffer prevents absorption if ambient NH_3 is present while the sample is in the autosampler.
- For IC: Add 10.0 ml of DDW to each filter sample in the extraction tube. For AC: Add 10.0 ml of 0.1 M sodium citrate to each filter sample in the extraction tube.
- For IC: Add 10.0 ml of DDW to one empty extraction tube and mark this tube as reagent blank. For AC: Add 10.0 ml of 0.1 M sodium citrate to one empty extraction tube.
- Cap the tubes tightly. Be sure that the exposed area on the filter remains completely immersed in the extraction solution.
- Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level.
- Measure the temperature. If the bath temperature is above 20 °C, add ice until it reaches at least 18.5°C. Record the temperature on the Extraction Data Log Sheet.
- Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at 30 minutes and at 60 minutes. If the temperature exceeds 25 ºC, add ice to bring the temperature down. (Caution: The water in the bath should be kept below 25 ºC.)
- Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1).
- Install the extraction rack on the shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3). Complete the entries on the DRI Filter Extraction Data Log Sheet (Table 2-1).
- Store the extracted samples in the refrigerator prior to chemical analysis. Complete the entries on the DRI Filter Extraction Data Log Sheet (Table 2-1).

5.0 QUANTIFICATION

(Not applicable.)

6.0 QUALITY CONTROL

For each batch of 40 samples being analyzed, analyze one extraction tube with extraction solution as a method blank. If the reagent blank is greater than the field blanks, another set of reagent blanks should be prepared, sonicated, shaken, and analyzed.

7.0 QUALITY ASSURANCE

(Not applicable.)

8.0 REFERENCES

None

APPENDIX A.7

DRI STANDARD OPERATING PROCEDURE

Pages: 31
Date: 3rd Quarter 2004
Number: 2-203.5
Revision: 5

Title: Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are to:

- provide a basic understanding of the principles of operating ion chromatography (IC)
- detail the implementation of a state-of-the-art ion chromatography measurement process, including interferences and technical problems that may arise while using the Dionex Series 500 Ion Chromatography (IC) System
- describe routine analysis of aqueous filter extracts of precipitation samples using the Dionex 500 Ion Chromatography System for the following anions:

Fluoride (F^-)
Chloride (Cl^-)
Nitrite (NO_2^-)
Bromide (Br^-)
Nitrate (NO_3^-)
Phosphate (PO_4^{-3})
Sulfate ($SO_4^{=}$)

This procedure will be followed by all analysts in the Environmental Analysis Facility, Division of Atmospheric Sciences, at Desert Research Institute.

1.2 Measurement Principle

Ion Chromatography (IC) using the Dionex 500 is a liquid chromatographic technique based on an ion exchange mechanism and suppressed conductivity detection for the separation and determination of anions. Its separation principle is similar to that of all chromatographic methods. Each ion's affinity for the exchange site, known as its selectivity quotient, is largely determined by its radius and its valence. As a consequence of differences in the equilibrium distribution of sample components between the mobile (sample/eluent flow) and stationary (ion exchange column) phases, the sample ions elute from the column as

discrete bands based upon their migration velocities. Each ion is identified by its retention time within the ion exchange column.

During routine operation, a filtered aliquot of sample is pumped through an ion exchange column where the ions are separated. The eluent ions from this separator column are then neutralized in the anion self-regenerating suppressor (ASRS) Ultra, and the sample ions are converted to their corresponding strong acids for detection with a conductivity detector. The conductivity responses are associated with ionic species by their elution times. Ionic concentrations are quantitatively determined from conductivity peak heights or area (Small et al., 1975).

1.3 Measurement Interferences and their Minimization

Water from the sample injection will introduce a negative peak or dip in the chromatogram when it elutes since its conductance is less than that of the suppressed eluent. Any ion of interest eluting near the water dip (such as F^- or Cl^-) must be sufficiently resolved from the dip in order to be accurately quantified. This can be achieved by changing the eluent concentration or decreasing the flow rate. Alternatively, the negative peak can be reduced by adding an equivalent of 100 mL of a prepared eluent concentrate (solution that is 100 times more concentrated than the eluent used for analysis) per 10.0 mL of sample. Proportionate eluent additions must also be included in calibration and quality control solutions (Bachman et al., 1986). Increasing the eluent concentration may, however, result in unresolved peaks or peak overlap.

The presence of air bubbles in the columns, tubing, or conductivity detector cell may cause baseline and peak variability. Introducing air into the system when injecting samples and standards should be avoided. The use of pressurized helium (He) with Dionex 500 IC should minimize the introduction of air bubbles to the system.

Unresolved peaks will result when the ion concentration of one of the sample components is 10 to 20 times higher than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or the flow rate may correct this problem. Decreasing the flow rate will, however, lengthen the retention time.

Interferences may be caused by ions with retention times that are similar to each other, resulting in overlapping peaks. Decreasing the eluent concentration or the flow rate may result in improved peak resolution and minimize the positive interferences (Bachman et al., 1986).

Injection of samples with total ionic concentrations greater than 50 µg/mL or the use of sample loop volumes greater than 250 mL may result in column overloading, causing the loss of the sample since it cannot be retained on an overloaded column. Non-quantifiable responses will also occur. Dilution of samples or decreasing the sample loop volume will prevent column overloading.

Column performance deterioration can result from the accumulation of contaminants on the exchange resin. Changes in retention times and in resolution are symptoms of column deterioration. Refer to the manufacturer's guidelines that are received with each new column (Dionex, 1991) or Section 2.1.3. for instructions on cleaning the column resin.

1.4 Ranges and Typical Values of Measurements

A wide range of ambient concentrations are found in both filter extracts and precipitation samples. Table 1-1 summarizes the ranges of anion concentrations from past DRI studies. "Typical" values are difficult to express except in terms of ranges, because µg/mL measurements depend on volume of extract or sample, amount of filter extracted, type of sample (i.e., urban or rural ambient, direct or diluted source), volume of air sampled, and filter deposit area. All of these factors may be adjusted to compensate for unusually low or high concentrations.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The Dionex 500 is capable of measuring the anions for F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{-3}, and SO_4 down to the 10 - 30 ppb range. The lower quantifiable limit (LQL) for each of the ionic species is determined by variability in blank analyses or the minimum detection limit - whichever is greater. Table 1-2 lists the LQLs resulting from various ion chromatography analyses. The accuracy is primarily limited by the uncertainties in the standard solution preparation and is typically within ± 5%. Precision as estimated by replicate analyses is in the range of ± 10% to ± 30%, depending on the analyte and the concentration of the analyte.

Table 1-1

Ranges and Typical Concentrations of Anions Determined by Ion Chromatography

	Dry Deposition ($\mu g/m^3$)	*Wet Deposition (μmole/ℓ)*	
Ionic Species	Ambient Concentration Range	Ambient Concentration Range	Typical Value
Cl^-	*0.15 to 0.22*[b]	*0.1 to 75*[a]	*0.5*[a]
NO_2^-	*3.0 to 44.0*[c]		
NO_3^-	*0.7 to 13.0*[c]	*0.2 to 14*[a]	*2.5*[a]
SO_4^-	*1.0 to 20.0*[c]	*0.1 to 8*[a]	*0.8*[a]

[a] *from Hidy et al. (1974)*

[b] *Range of average fine particle values at urban and nonurban sites from Watson et al. (1981)*

[c] *Preliminary data from CADMP sites for PM_{10} samples (Watson et al., 1989)*

Table 1-2

Lower Quantifiable Limits of Anions Determined by Ion Chromatography

	Lower Quantifiable Limits	
Ionic Species	($\mu g/m^3$)[a]	µg/ml
F^-	*0.0017*	*0.05*
Cl^-	*0.0017*	*0.05*
NO_2^-	*0.0017*	*0.05*
NO_3^-	*0.0017*	*0.05*
SO_4^-	*0.0017*	*0.05*
Br^-	*0.0017*	*0.05*
$PO_4^=$	*0.0017*	*0.05*

[a] *Values given are per filter assuming no dilution factor, 10 ml extraction volume, and sampling at 33 1/min for 24 hours*

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure before performing IC analysis. The analyst is expected to follow this procedure step by step to perform routine system calibrations, chemical analyses, and performance tests. The laboratory manager is responsible for ensuring that the IC procedures are properly followed; to examine all replicate, standard, and blank performance test data; to designate samples for re-analysis; and to deliver the analysis results to the project manager within the specified time period.

The EAF quality assurance (QA) officer is responsible for determining the QA methods to be applied to each project; estimating the level of effort required for QA; identifying the appropriate personnel to perform QA tasks; updating QA procedures; and assuring that QA tasks are budgeted and carried out as part of contract performance.

1.7 Definitions

The following terms are used in this document:

Analytical Column/Separator Column	The column used to perform the actual chromatographic separation.
Column Capacity	Related to the total ionic strength of the sample, it is the maximum concentration of sample that may be loaded onto a separator column before overloading occurs.
Conductivity	A measure of the characteristic of ions in solution to carry electrical current through a liquid between two oppositely charged electrodes. When combined with chemical celuent suppression, it provides excellent selectivity and sensitivity for many ionic species.
Eluent	The ionic liquid mobile phase used to transport the sample through the guard and analytical columns.
Guard Column/Pre-Column	A small column that prevents poisoning and contamination of the separator column by removing particles and absorbing organic compounds.
Ion Exchange	The reversible process by which ions are interchanged between an insoluble material and a liquid with no substantial structural changes of materials.
Ion Exchange Capacity	The number of active ion-exchange sites in a given weight or volume of resin, often expressed in meq/g or meq/mL.
Ion Exchange Resin	An insoluble carbon-based polymer matrix containing charged exchange sites (anionic or cationic). The resin used in IC is formed into small spherical particles (i.e., beads).

ASRS Ultra	A device used to continuously minimize eluent conductivity and convert sample species to a high conductivity form, thus increasing detection sensitivity.
Resolution	A measure of the ability of a column to separate constituents under specified test conditions. Peak resolution is a function of column efficiency, selectivity, and capacity.
Retention Time	The interval measured from the point of sample injection to the point of maximum peak height or area; the basis for identification of a species in chromatography.
Theoretical Plates/Column Efficiency	A measure of peak dispersion as flow moves through a column proportional to column length for a given column diameter and resin.

1.8 Related Procedures

Related laboratory procedures are specified in the following DRI Standard Operating Procedures:

DRI SOP 2-104.3	Impregnation and Drying of Filters for Sampling Gases in Air
DRI SOP 2-108.4	Filter Sectioning
DRI SOP 2-109.5	Extraction of Ionic Species from Filter Samples

2.0 APPARATUS, INSTRUMENTATION, AND REAGENTS

2.1 Apparatus and Instrumentation

2.1.1 Description

The Dionex 500 is a completely inert and metal-free analytical system. The system is composed of an isocratic pump, a chromatographic column, a continuously regenerated suppressor (ASRS), a detector system, and an autosampler.

The Dionex 500 system includes:

Pump Module: A microprocessor-based eluent delivery system designed to provide isocratic or gradient elution capability at precisely controlled flow rates. It is a dual-piston, direct current (DC) motor pump that can be operated with flow rates ranging from 0.04-10.0 mL/min (in increments of 0.01 mL/min) and pressures ranging from 0 to 5000 psi.

Eluent Degas Module: Provides continuous on-line purging, degassing, and pressurization of as many as four eluent reservoirs with He gas.

Sampling System: Samples are introduced into the analyzer with either an automated sampler or a hand-operated syringe.

-- Automated Sampler: Can be operated manually from the front panel or remotely from the computer. In routine operation, the automated sampler system is used to deliver between 2.5 and 5.0 mL of sample through the 250 µL sample loop. The sampler compartment can hold up to 66 5.0mL or 88 0.5mL vials (including quality control samples). Each PolyVial sample vial is equipped with a 20 µm filter cap to remove particulates from the sample before injection and to prevent contamination or loss of the sample through evaporation or spills. The filter cap also serves as a piston to force samples out of the vial.

-- Syringe: A polyethylene syringe with a minimum capacity of 1 mL is used for manual injection of samples. The syringe is equipped with a pre-filter for use with samples that contain particles.

Advanced Chromatography Module: A dual hydraulic system that contains an injection valve (a high-pressure pneumatically operated six-port valve with a 250 µL sample loop), two columns, a conductivity detector cell, and inter-connecting tubing.

Figure 2-1 illustrates the flow through the Advanced Chromatography Module. Pumped eluent and sample are mixed at the injection valve. The mixture of eluent and sample then flows through the guard column, through the separator column, through the ASRS, and finally through the detector cell to waste.

ASRS Ultra: A device used to continuously minimize eluent conductivity and convert sample species to a high-conductivity form, thus increasing detection sensitivity.

Conductivity Detector: A microprocessor-controlled detection system based on electronic signal processing to increase the signal-to-noise ratio and enhance sensitivity at low concentrations. The system displays conductivities over the full-scale range of 0.01 to 1,000 µS (micro Siemen) and compensates for temperature-induced conductivity variations, with correction factors between 0.0 and 9.9% per °C.

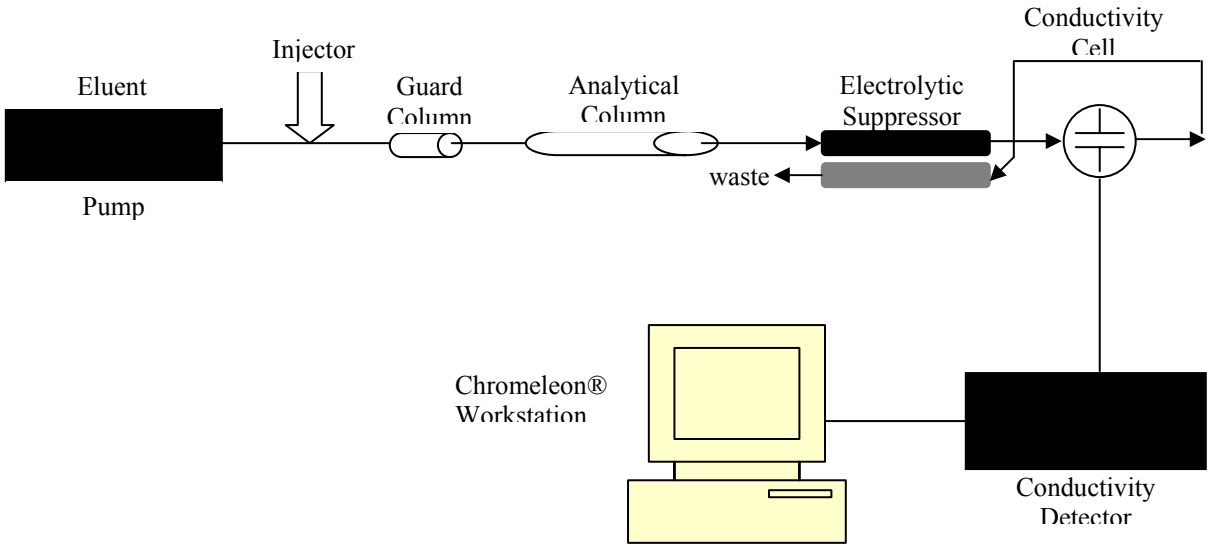


Figure 2.1. Flow schematic for anion analysis by the Dionex 500 Ion Chromatography System.

2.1.2 Characterization

The Dionex 500 equilibrates about 15 minutes after the appropriate anion method has been entered and the pumps have started. The instruments are stable and will produce area counts within ±10% of previous readings, dependent upon the primary standard used to make up the calibration standards and the eluent solution used.

2.1.3 Maintenance (Consult the Dionex 500 Operator's Manual)

Column. Clean the column if there are significant changes in component retention times. The columns are disconnected from the ASRS, their positions reversed with the guard column after the analytical column. Next, eluent is pumped through the columns directly into a waste container. After 30 minutes, replace the column bed supports, connect the columns in their proper order, reconnect to the ASRS, and equilibrate the complete system before continuation of sampling.

Conductivity Detector. Conduct periodic leak checks of the liquid line connections to the cells;, the unit itself is not user serviceable.

Pump. Replace the check valves, piston seals, and washer support seals each year or when there is excessive leakage from the pump valves.

2.2 Reagents

The following chemicals should be American Chemical Society (ACS) reagent grade or better:

Sodium bicarbonate ($NaHCO_3$)
Sodium carbonate (Na_2CO_3)
Sodium fluoride (NaF)
Sodium chloride (NaCl)
Sodium nitrite ($NaNO_2$)
Sodium bromide (NaBr)
Sodium nitrate ($NaNO_3$)
Sodium phosphate (Na_2HPO_4)
Sodium sulfate ($NaSO_4$)

2.2.1 Water

Use water conforming to American Society for Testing Materials (ASTM) Specification D 1193, Type II (ASTM Standards, 1982). Deionized-distilled water (DDW) having a resistance of at least 18 megohm per cm, is required for all analyses.

2.2.2 Eluent Solution

Using the AG14 guard column and the AS14 analysis column, 0.0010 M $NaHCO_3$/0.0035 M Na_2CO_3 solutions are used to elute ions from the separator/analytical column.

These are prepared by using the following procedures:

Stock Solutions:

0.1 M Sodium Bicarbonate ($NaHCO_3$):

Weigh 8.40 g $NaHCO_3$ into a disposable weighing boat. Transfer quantitatively to a 1000 mL volumetric flask containing approximately 800 mL DDW by rinsing it into the flask with distilled-deionized water (DDW) from a wash bottle and dissolve completely. Bring to volume with DDW.

0.1 M Sodium Carbonate (Na_2CO_3):

Weigh 10.60 g Na_2CO_3 into a disposable weighing boat. Transfer quantitatively to a 1000 mL volumetric flask containing approximately 800 mL DDW by rinsing it into the flask with DDW from a wash bottle and dissolve completely. Bring to volume with DDW.

Eluent Solution:

0.0010 M $NaHCO_3$ and 0.0035 M Na_2CO_3 combined eluent:

Using a grade A graduated cylinder, measure 80.0 mL 0.1 M $NaHCO_3$ into the 10 L carboy, then measure 280.0 mL of 0.1 M Na_2CO_3 into the same carboy. Fill to the 8 L mark with DDW. Mix. Pour this solution directly into the eluent reservoirs located on top of the conductivity module.

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

The stock standard solutions should either be purchased as certified solutions or prepared from ACS reagent grade materials. These solutions should be properly labeled with the name of the chemical, concentration, initials of the analyst, and the date it was prepared.

3.1.1 Preparation of Stock Solutions (1000 µg/mL)

A combined stock solution containing the analytes of interest is prepared from ACS reagent grade chemicals. The stock solution is approximately 1000 µg/mL of each of the components of interest, to four significant figures. Discard solutions after 1 year.

The solid reagent chemicals should be dried at 105°C for 1 hour and cooled in a dessicator. Care must be taken when weighing chemicals not to loose solid reagent because of static electricity.

- Chloride (to be 1000 µg/mL in the combined stock):

  Use NaCl, assaying at 100%. (Sodium Chloride, Baker Analyzed Reagent, #3624-1, 500 g bottle. J. T. Baker Chemical Co. Phillipsburg, N. N.J. 08865)

  Weigh 0.8243 g NaCl (to the nearest 0.1 mg) into a disposable weighing boat. Transfer quantitatively to a 500 mL volumetric flask by rinsing with DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

- Nitrite (to be 1000 µg/mL in the combined stock):

  Use $NaNO_2$, (Sodium Nitrite, Crystals, #SX0665-1, 500 g bottle. EM Science, Gibbstown, N.J. 08027)

  Correct the weight used by the assay value of nitrite. If the assay were 100%, 0.7535 g would be needed. Divide this value by the fraction assay to calculate the required amount; e.g.:

  97.4% pure $NaNO_2$ requires 0.7535/0.974 g = 0.7736 g $NaNO_2$

Weigh the calculated amount (to the nearest 0.1 mg) into a disposable weighing boat. Transfer quantitatively to the same 500 mL volumetric flask by rinsing it into the flask with DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

- Nitrate (to be 1000 µg/mL in the combined stock):

  Use $NaNO_3$ assaying at 100%. (Sodium Nitrate, Crystals, #SX655-1, 500 g bottle. EM Science, Gibbstown, N.J., 08027.)

  Weigh 0.6854 g $NaNO_3$ (to the nearest 0.1 mg) into a disposable weighing boat. Transfer quantitatively to the same 500 mL volumetric flask by rinsing it into the flask with DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

- Sulfate (to be 1000 µg/mL in the combined stock):

  Use Na_2SO_4, assaying at 100%. (Sodium Sulfate, Anhydrous, Fisher Scientific #S421-500, 500 g bottle. Fisher, Fair Lawn, N.J. 07410.)

  Weigh 0.7425 g Na_2SO_4 (to the nearest 0.1 mg) into a disposable weighing boat. Transfer quantitatively to the same 500 mL flask by rinsing it into the flask with DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

- Phosphate (to be 1000 µg/mL in the combined stock):

  Use Na_2HPO_4, assaying at 100%. (Sodium Phosphate, Dibasic, Anhydrous, Baker Analyzed, #3828-1, J.T. Baker Co., Phillipsburg, NJ, 08865)

  Weigh 0.7534 g Na_2HPO_4 (to the nearest 0.1 mg) into a disposable weighing boat. Transfer quantitatively to the same 500 mL flask by rinsing it into the flask with DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

  Dissolve the combined salts in approximately 400 mL DDW and dilute to volume with DDW. Mix thoroughly.

  Store the stock solution in a clean plastic 500 mL bottle by rinsing the bottle three times with the stock solution to remove any water or other contaminants from the storage bottle. Rinse the screw cap with stock solution also. After rinsing is complete, pour the stock solution into the

plastic storage bottle. Label the storage bottle clearly with the contents, the date of preparation and the initials of the person who prepared it. Store the stock solution in the refrigerator.

Concentrations are calculated according to the formula:

$$W_s = (C_s)(g/10^3 \text{ mg})(10^3 \text{ mL/L})(0.500 \text{ L}) * \frac{(FW_s)}{(FW_x)} * \frac{100}{\%assay}$$

where:

W_s	=	the weight of the salt in stock standard in g.	
C_s	=	the concentration of the stock solution in mg/mL.	
$(FW)_s$	=	the formula weight of the salt s in grams.	
$(FW)_x$	=	the formula weight of ion x in grams.	
% assay	=	the purity of the salts of an ion x in percent.	
0.500 L	=	the volume of combined stock prepared.	

3.1.2 Preparation of Working Standards (100 µg/mL and 10 µg/mL)

The stock solutions above are diluted to two working standards, which are used to prepare calibration standards. The same calibration standards are used each day as QA during every analysis run.

- 100.00 µg/mL working standard: Pipet 10.00 mL (using grade A pipet) of the combined stock solution (1000.00 mg/mL) into a 100.00 mL volumetric flask. Dilute to volume with DDW. Actual concentrations are calculated by dividing the actual concentration of the stock (C_s) by 10.

- 10 µg/mL working standard: Use a grade A pipet to transfer 10.00 mL of the 100.00 mg/mL working solution into a 100.00 mL volumetric flask. Dilute to volume with DDW. Actual concentrations are calculated by dividing the concentration of the stock (C_s) by 100.

3.1.3 Preparation of Calibration Standards

These are the standard solutions used to create the calibration curves for the analysis. The concentrations are as follows:

Working	Volume of Working	Final

Concentration	Standard	Standard	Volume
0.05 µg/mL	10 µg/mL	0.50 mL	100 mL
0.1 µg/mL	10 µg/mL	1.00 mL	100 mL
0.2 µg/mL	10 µg/mL	2.00 mL	100 mL
0.5 µg/mL	10 µg/mL	5.00 mL	100 mL
1.0 µg/mL	10 µg/mL	10.00 mL	100 mL
2.0 µg/mL	100 µg/mL	2.00 mL	100 mL
3.0 µg/mL	100 µg/mL	3.00 mL	100 mL

The standards are checked every Monday using the same sequence as the standard curve and remade when the volume available is not sufficient for the week, usually every two weeks during routine operation.

3.2 Use of External Quality Control Standards

Stock solutions prepared from ACS reagent grade materials should be cross-examined with certified solutions as a quality control (QC) check. QC standards may be purchased from Environmental Resources Associates (ERA), Dionex, or Alltech Associates, Inc. The concentration of the ions is 100µg/mL.

Prepare a secondary stock solution at 10 µg/mL by diluting the ERA or the Alltech stock solution. Prepare the working standards as follows:

- 1.00 µg/mL QC, ERA or Alltech:

Using a 10.0 mL class A pipet, pipet 10.00 mL of the 10 µg/mL secondary stock into a 100.00 mL volumetric flask. Bring to volume with DDW and mix thoroughly.

- 0.100 µg/mL QC, ERA or Alltech:

Using a class A pipet, pipet 1.0 mL of the 10 µg/mL secondary stock solution into a 100 mL volumetric flask and bring to volume with DDW.

The following are further control checks for ions of interest:

- *ERA Minerals WasteWatR standard is used as a QC check for routine analysis of chloride and sulfate. Every standard solution is supplied with documentation concerning concentrations. A concentration that is within range of the calibration is calculated and the standard is diluted accordingly.*

- *ERA Nutrients WasteWatR standard is used for routine analysis of nitrate and phosphate. Every standard solution is supplied with documentation concerning concentrations. A concentration that is within range of the calibration is calculated and the standard is diluted.*

3.3 The Accuracy of Calibration Standards

The accuracy of calibration standards is primarily limited by the uncertainties or variabilities of the standard solution preparation and is typically within ±10%.

4.0 PROCEDURES

4.1 General Flow Diagram for the 500 system.

Figure 4-1 describes the general flow diagram for filter chain-of-custody, chemical analysis, and data processing/validation. Figure 4-2 shows an example of DRI's analysis list. Figure 4-3 describes the general flow diagram of routine ion chromatography analysis, starting with the initial chromatography adjustment and analysis parameter setup. The samples and replicates are analyzed after the calibration curve is established.

Figure 4-1. Flow activities in the Environmental Analysis Facility.

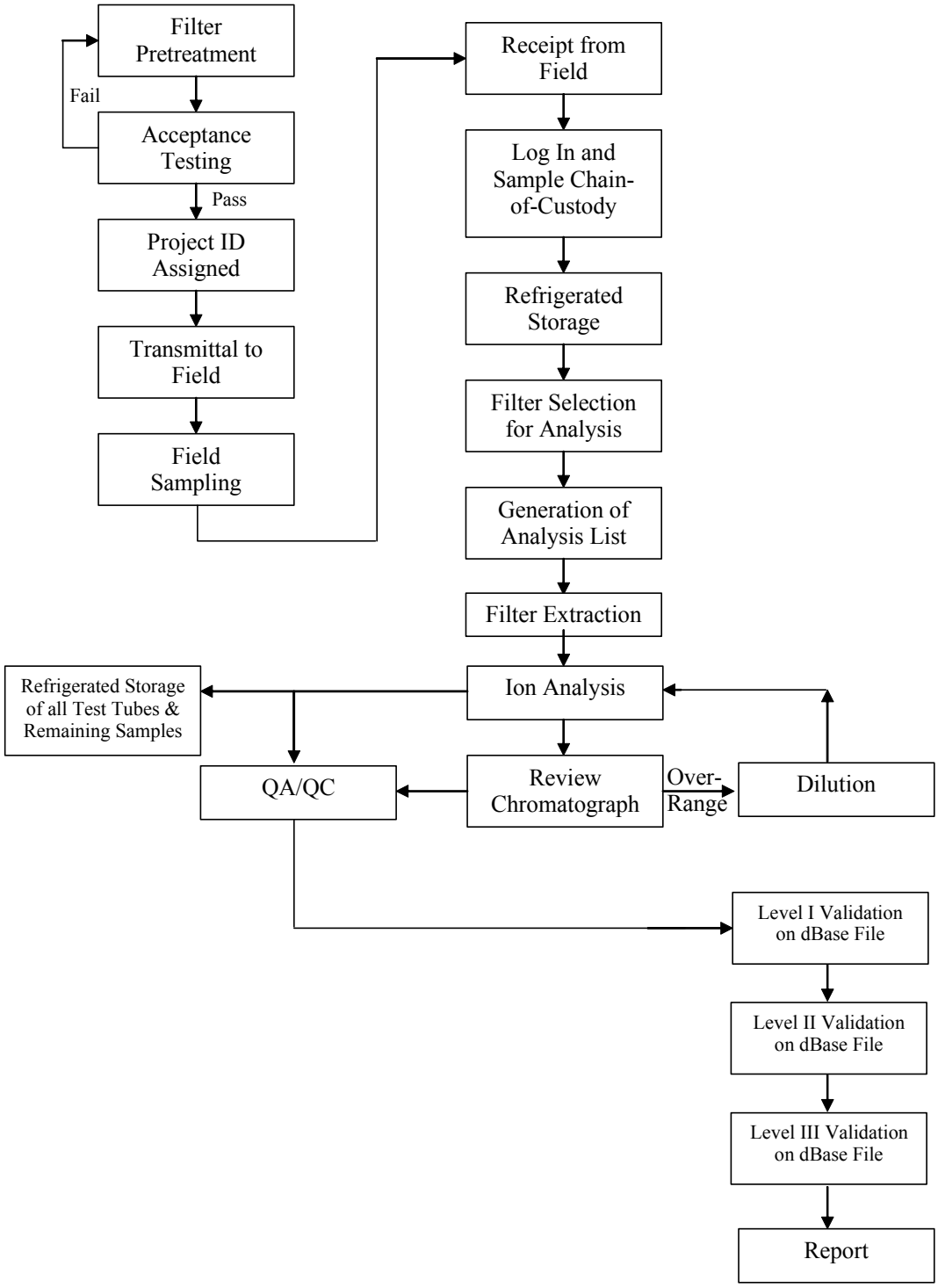


Figure 4-2(a). Example DRI analysis list – (a) page 1 - analysis information

Vegas 2002: Batch Ø1 Quartz

Date : Ø3/17/Ø3 Account: - -

From : S. Kohl

To : J.Chow
D.Crow
J.Watson
Carbon Lab
IC Lab
AC Lab
AA Lab

Analysis:	OC/EC	by TOR : 46 samples, data in VCOETØ1S.DBF
	Cl-/NO3-/SO4=	by IC : 46 samples, data in VCANIØ1S.DBF
	NH4+	by AC : 46 samples, data in VCN4CØ1S.DBF
	K+	by AA : 46 samples, data in VCKPAØ1S.DBF
	Na+	by AA : 46 samples, data in VCNAAØ1S.DBF

Sample Overview:

This analysis list covers samples from the Mark Green Ambient sampling network project. These are 46 PM2.5 samples on 47 mm Quartz filters, including no lab blanks and no field blanks. These samples were collected with a SFS sampler.

Analysis Overview:

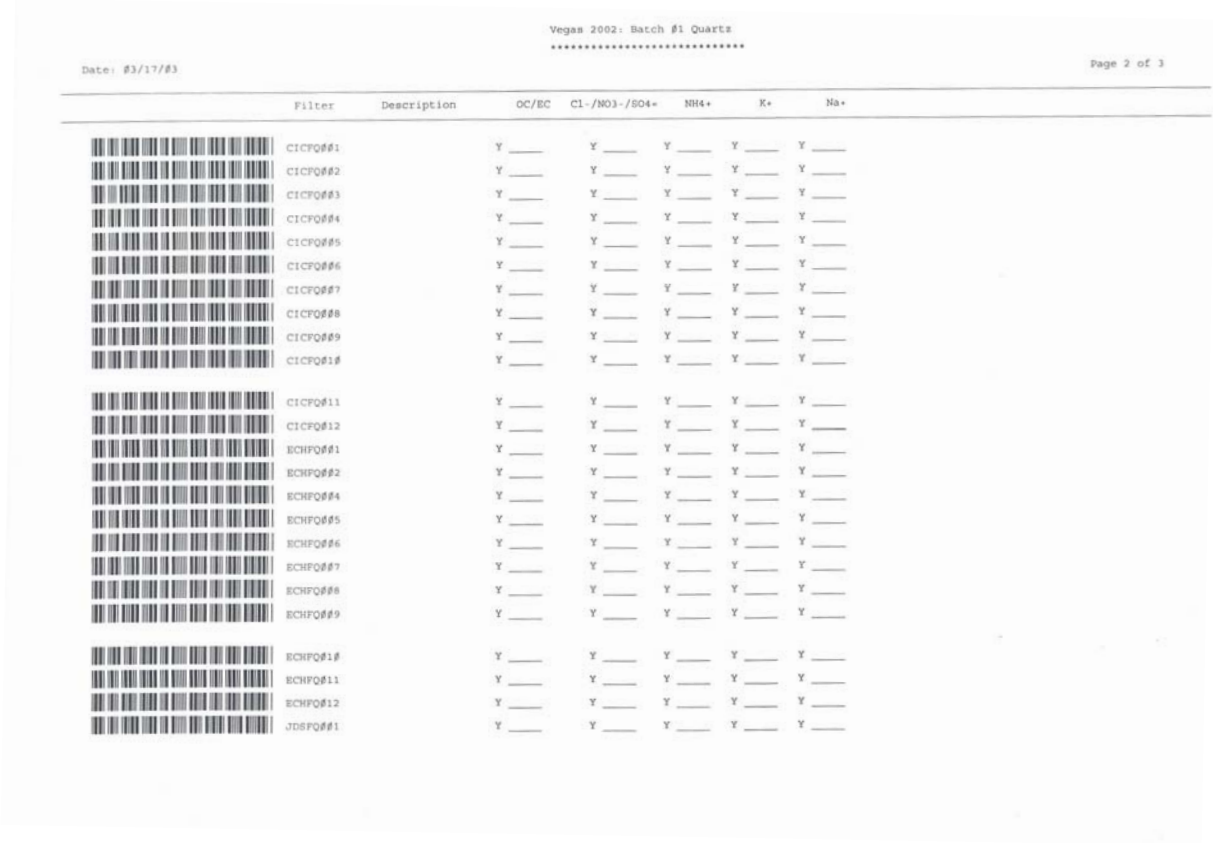
Sample deposit area: 13.8Ø cm^2
Analysis start date: ASAP
Analysis deadline : 4/1/Ø3
Sample location : Shipping/receiving

Analysis Details:

Sample extractions must be scheduled with Wet Chem Lab personnel. Samples will be quantitatively halved and extracted in 15.Ø ml DDW. Samples will be sonicated for 6Ø minutes, shaken for 6Ø minutes, and left in the refrigerator overnight before analysis begins. Analysis data will be stored in the \VEGAS.Ø2\BATCHØ1 directory.

Carbon analysis data will be stored in the D:\VEGAS.Ø2\BATCHØ1 directory.

Figure 4-2(b). Example of DRI analysis list – (b) page 2 - barcoded IDs for all samples to be analyzed.



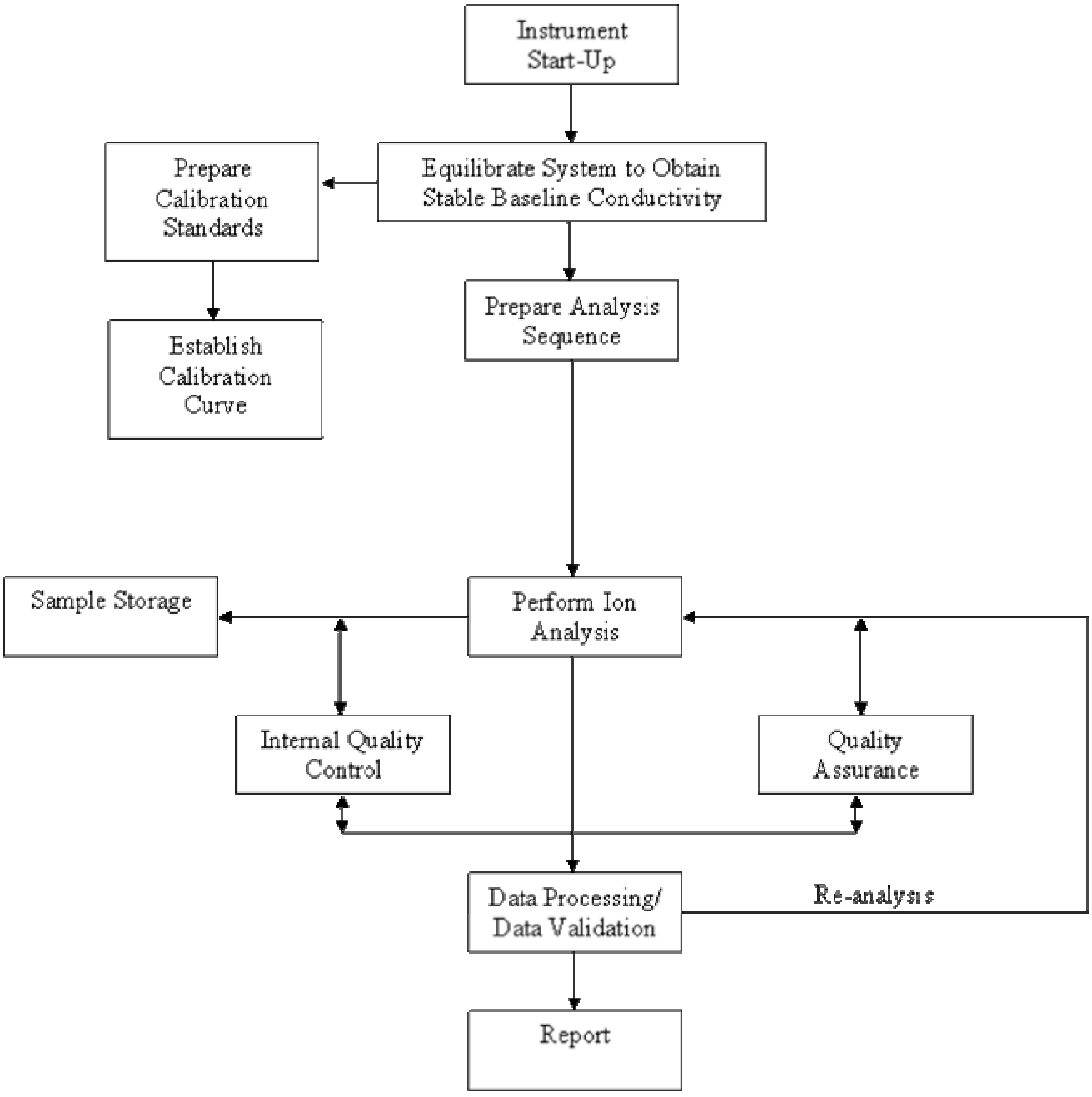
Vegas 2002: Batch #1 Quartz

Date: #3/17/#3

Page 2 of 3

Filter	Description	OC/EC	Cl-/NO3-/SO4=	NH4+	K+	Na+
CICFQ##1		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##2		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##3		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##4		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##5		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##6		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##7		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##8		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ##9		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ#1#		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ#11		Y ____	Y ____	Y ____	Y ____	Y ____
CICFQ#12		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##1		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##2		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##4		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##5		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##6		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##7		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##8		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ##9		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ#1#		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ#11		Y ____	Y ____	Y ____	Y ____	Y ____
ECHFQ#12		Y ____	Y ____	Y ____	Y ____	Y ____
JDSFQ##1		Y ____	Y ____	Y ____	Y ____	Y ____

Figure 4-3. Flow diagram for IC analysis.



4.2 Startup for the Dionex 500 Software and Instrumentation

4.2.1 Software: Chromeleon (CM) Startup

- Start the Server Monitor. The server monitor can be found either in the CM startup menu or in the lower right corner of the desktop. After the server monitor has been started, click Close, which will save the icon on the Windows Services area of the task bar.

- Start Chromeleon from the desktop shortcut. It will open to the browser (Fig 4.2.1). Select the anion ("Bubbles") timebase in the left frame of the browser (Figure 4-4).

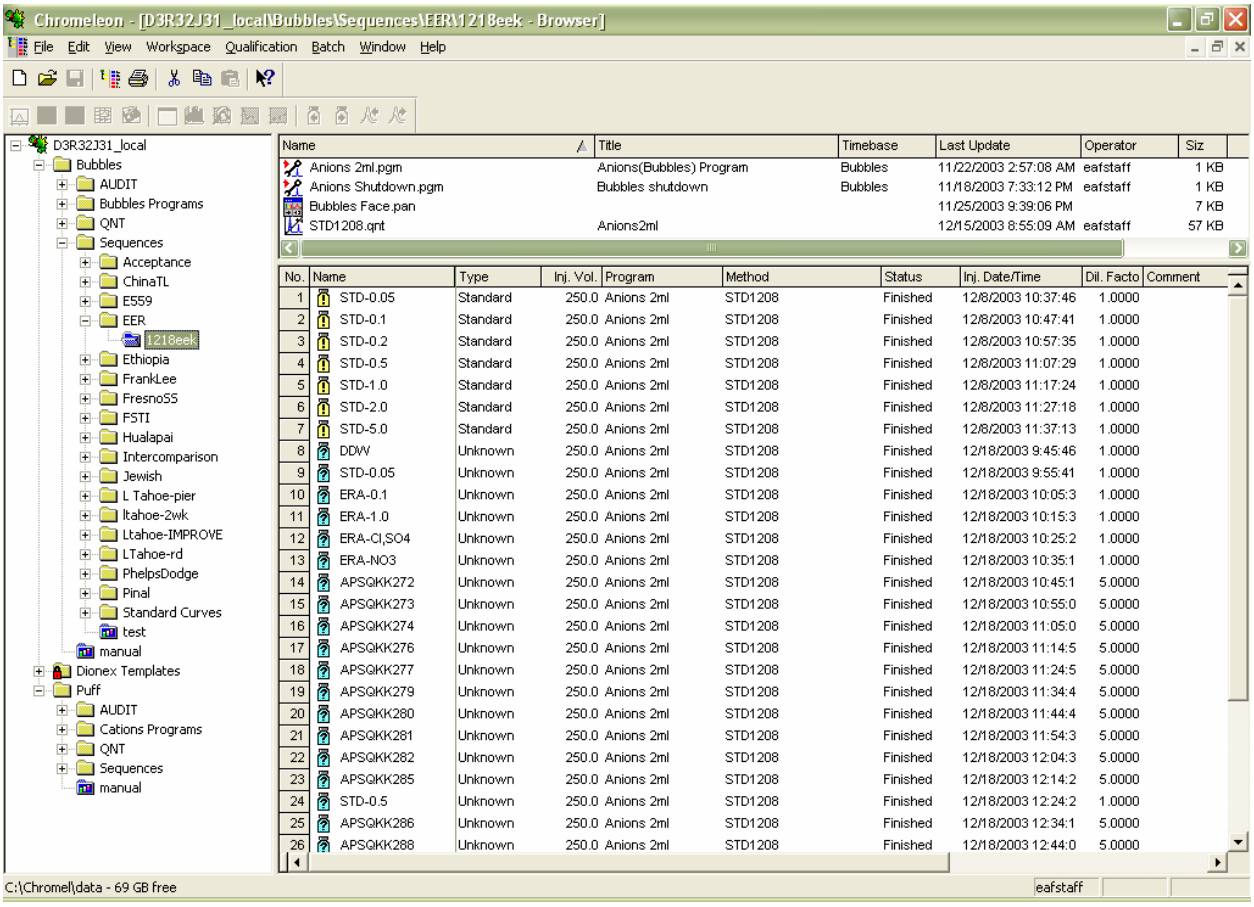


Figure 4-4. Browser window with the anion timebase (“Bubbles”) in the left frame, the programs and .QNT method in the upper right frame, and a sequence in the lower right frame.

4.2.2 Hardware Startup/Shutdown

- In the browser window, click on the bubbles folder, then click on Bubbles Face.pan. The control panel face will appear. (Figure 4.5)

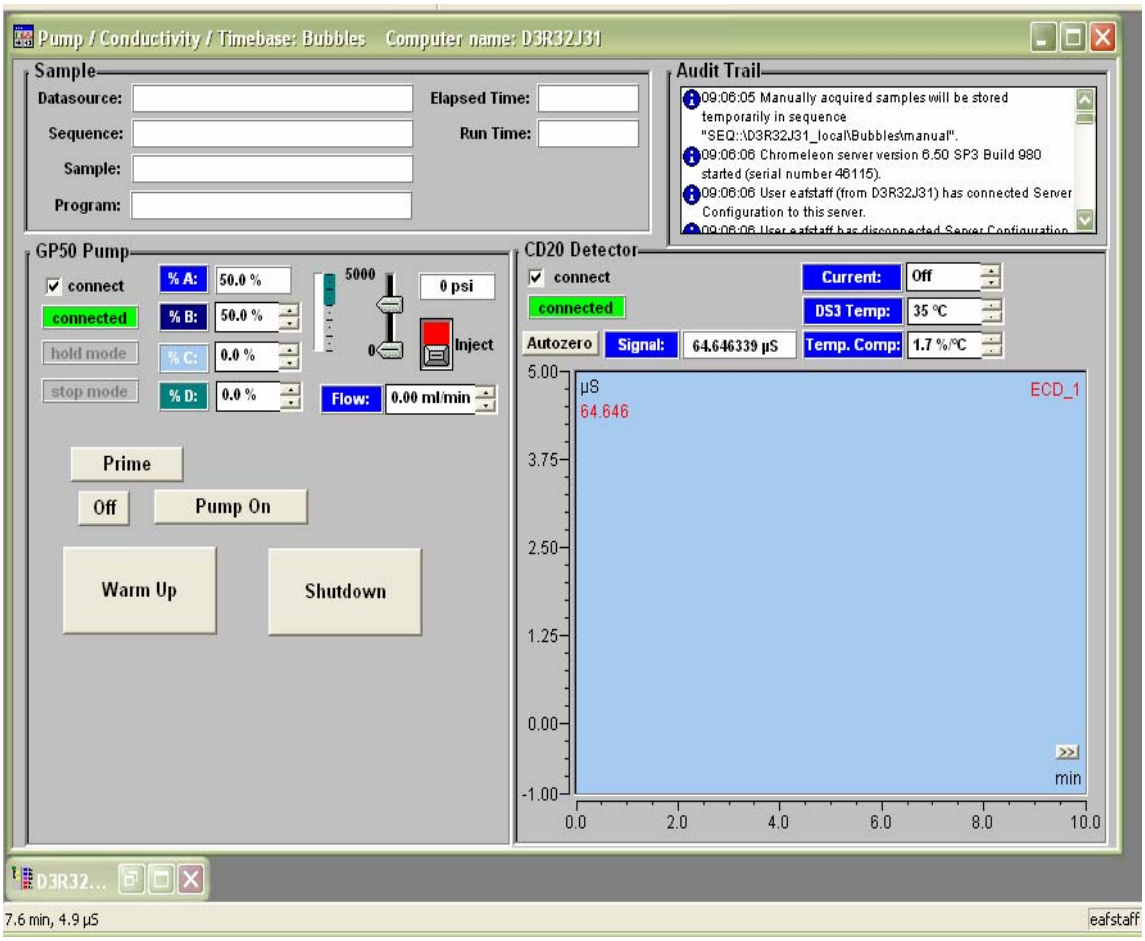


Figure 4-5. Example of the panel face with the warm up and shutdown buttons.

- Startup: Click on the **warmup** button on the panel face. The pumps and detector will turn on. Figure 4-6 delineates the commands that are contained in this button.

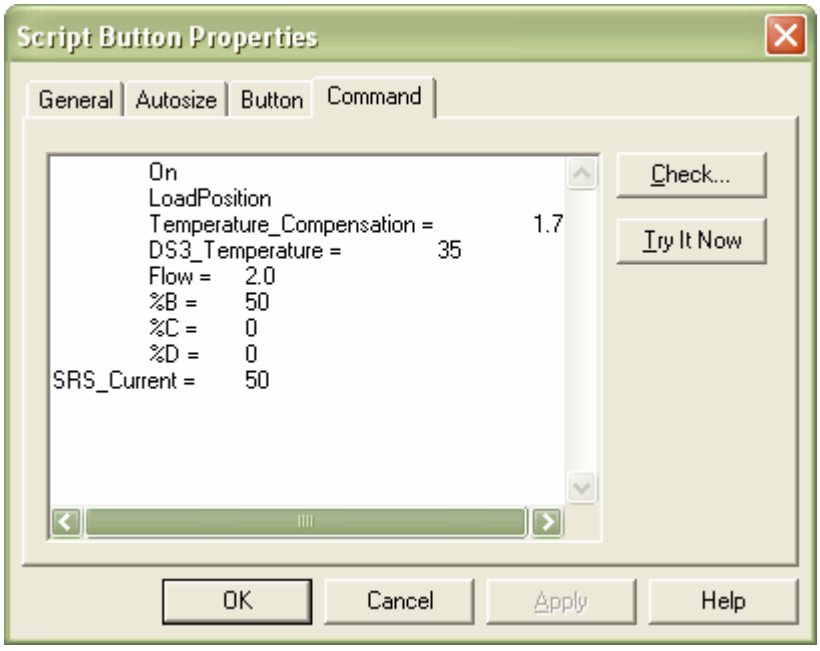


Figure 4-6. Warmup commands.

- Shutdown: Click on the **shutdown** button on the panel face. The pumps and detector will turn off. Figure 4-7 delineates the commands that are contained in this button.

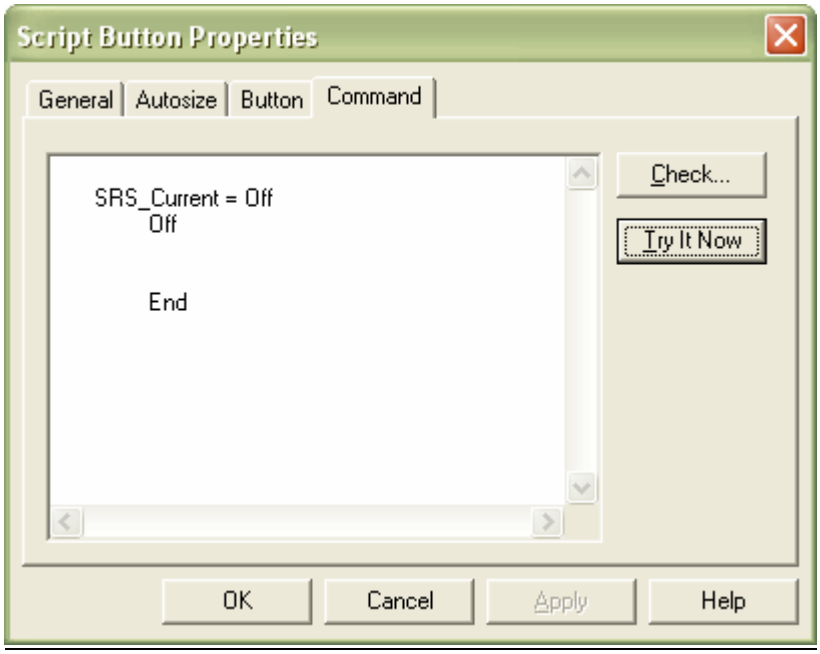


Figure 4-7. Shutdown commands.

- Manual shutdown of the hardware and software if the system locks up:

1. Push Hold **button on AutoSampler AS40.**

2. Turn the modules CD20 and GP50 off.

3. Exit the software and **quit** the Chromeleon Server in the bottom status bar.

4. Turn the computer off.

- Manual startup if the hardware and software are already off:

1. Turn on Modules CD20 and GP50

2. Turn on the computer

3. Proceed with the software startup procedure described in 4.2.1

4.2.3 Creating a Sequence

- From the browser, click File and select New. Select Sequence (using Wizard) and follow further instructions, **OR**

- From the browser, open a previously created sequence template and save the sequence to the new name. The sequence **status** column will change from "finished" to "single" (Fig.4.4). Modify the sample name, sample type, position, program, method, and comment (field blanks, replicates, etc.) as listed on the analysis list.

- Copy and paste the standards used in the generation of the .qnt in use. Click **Include Raw Data** when pasting. The standards are ordinarily placed first in the sequence, but can be added anywhere.

4.2.4 Creating a Quantification Method (Standard Curve)

- From the browser, click **File** and select **New**. Select **Method File** from the Wizard dialog box. The Method Editor opens with the general tab sheet displayed. Title the method with the current date.

- Click the **Detection** tab. **Minimum Area** is listed with a "value" of 0.000. Using the drop-down, change this to **Detect Negative Peaks** with a "value" of **On-Don't label**. Save the method to the QNT folder as "MonthYear" and **exit** the Method Editor.

- Create a sequence using the Wizard (see 4.2.3) that contains the concentrations chosen for the standard curve. The **Method** will be the one just created with the method wizard and which is stored in the QNT folder.

- Start the sequence from the open browser window. Select **Batch**, **Ready Check**, and **Start** if there are no error messages. Any error message needs to be resolved before starting the batch.

- When the sequence has ended, open any standard in the run. Click the QNT icon on the menu bar.

- Several baseline noise peaks may be integrated with the main peaks. To eliminate the extra peaks, select the **Detection** tab and add **Minimum Area** with a "value" of 0.001.

- Click the **General** tab, enter "µg/mL" in the **Dimension of Amounts** field and confirm that **Auto Recalibrate** box is checked.

- Click the **Peak Table** tab, right-click on the gray half of the window and choose **Autogenerate Peak Table**. Choose **Enumerate Peaks of Current Chromatogram**. Read warning and answer **OK** when it appears on the next screen. Type in peak names for listed peaks as they elute from the column.

- Click the **Amount Table** tab, right-click in the empty gray space, select **Columns**, then select **Edit Columns.** Select **Autogenerate**, then select **One for each peak**. Enter values for each level of standard in the amount columns, as indicated. Use F9 to copy the values down the column.

- Click the **Detection** tab, set the integration parameters as needed. Detection parameters serve to recognize, classify, or suppress peaks, and to determine the baseline contact.

- Click the **Calibration** tab. If any standard is deemed unsuitable, the enabled box can be unmarked. Answer the question on the ensuing window. A red star in the calibration curve will indicate standards that are not included.

- Click the **Peak Area** tab to fit the new curve as linear, quadratic, or cubic; in most cases, it is linear to the 2.0 µg/mL standard; after that standard, a quadratic curve may be considered suitable.

- From the title bar, Select **View** then **Show Report**. Scroll through each standard using the forward and reverse arrow icons to verify the amounts in each run. The correlation for each analyte should be 99.7% or greater.

- Save the Method File (Standard curve) in the QNT folder for further use.

- Run a set of working standards each Monday to check their values. This is done by adding them to the sequence for the standard curve generated above. A curve is good as long as the retention times do not change much; if they do change and appear outside of the retention window, the curve will need to be regenerated, as above. If the working standards and the QC samples give acceptable results, the curve does not need to be regenerated.

- The detection parameters in the .qnt (method) can be modified in each run depending on the nature of the samples. This .qnt file then becomes embedded in the samples of the particular sequence.

4.3 Routine Operation

4.3.1 Initial Chromatograph Adjustment, Daily Operation

Ensure the following:

- Eluent bottles are filled with the carbonate/bicarbonate solutions.
- Helium tank pressure is greater than 500 psi, with a delivery pressure of 7 psi. Helium is inert and will keep ambient air out of the system.
- The compressed air tank pressure is greater than 500 psi, with a delivery pressure of 100 psi.
- The DDW reservoir is set at 7 psi.

Perform the following steps:

- Use the pressure regulators on the front of the DDW container to pressurize. Pump eluent for 15-20 minutes or until the conductivity stabilizes
- Take the working standards out of refrigerator, and prepare fresh standards if the quantities are insuffiecient for the run.

The conductivity should stabilize between 15 and 18 microSiemens. If the conductivity is not within these limits, check for leaks; air bubbles may cause variation. (See troubleshooting.) The pressure should stabilize between 2200 and 2800 psi.

- While the instrument is stabilizing, generate the report for the previous day's analyses, make working standards (if necessary), generate the day's run schedule, and load samples into autosampler vials.

4.3.2 Sample Analysis

Prepare the sequence. Use the Wizard (see 4.2.3) or copy a finished sequence and save it under a new name. The naming convention is mmddppxy (month, day, project, type and tray). If using the Wizard, the number of vials will equal the number of samples plus 10%. The sample ids and standards are entered into the final generated or copied sequence. In the new sequence, all **status** will be "single" (no data yet).

- Copy the standards used to generate the .qnt (method) into the system; click on **Save Raw Data.** When they are properly copied, "finished" will appear in the **status** column.

The next samples in a run are always the QC samples, in this order:

DDW
STD-0.05 (µg/mL)
ERA-0.1 (µg/mL)
ERA-1.0 (µg/mL)
ERA-Minerals
ERA-Nutrient

Samples are run in-groups of 10, followed by a standard. After 20 samples, a blank and a standard are analyzed. Thus, after the QC entries in the schedule, the sample schedule will have the format:

10 samples
1 replicate
1 standard
10 samples
1 replicate
1 DDW
1 standard

The concentration of standards in the sequence usually starts with the 0.1 µg/mL and increases sequentially through 5.0 µg/mL. If the run is very short, a random selection may be used. The above pattern repeats until all of the samples have been analyzed. At the end of the final pattern, add the method blank(s). Because the final sample in every run must stop the run, its name will be STOP with **Anions Shutdown** program chosen. The **Shutdown** program turns off the conductivity detector and the pump.

- Click on **File**, **Print Sequence** to print a hard copy of the sequence to use when loading the samples. Fill sample vials with approximately 2 mL of each solution indicated on the sequence. Place the sample vials in the tray with the first sample at the end with the black dot. This will align the tray with the belt in the autosampler. Cap the vial with filtered caps by inserting the cap into the tube with the narrow part up and pushing the cap to the level of the tray with the push-tool..

- Place the cassettes into the autosampler by sliding the spring-loaded cassette pusher back and inserting the cassette into the autosampler tray with the black dot to the right. Select **Run** on the front console of the autosampler. The tray will move into position.

- Start the analysis from the open browser window. Select **Batch**, **Start**. Click on **Ready Check** to verify that there are no errors in the run. " Ready Check OK" indicates no problems. All error messages should be resolved before beginning the run.

- Click on **Start** to begin the run. The autosampler will start; listen for the piston to descend. The autosampler bleeds off the first 2.5 mL volume (air), then slowly injects the rest of the sample. It takes approximately 2 minutes for the probe to go all the way down.

4.4 Shut-Down

4.4.1 Routine Instrument Shut-Down

- A STOP sample is used at the end of the sequence in every run. Use the **Anions Shutdown** method in the program column.

OR

- Press the **Shutdown** button on the panel face to turn off the pump and detector.

4.4.2 Waste Disposal

- Pour the waste into the sink. The solution is the buffered carbonate-bicarbonate eluent.

4.5 CHECKLIST

- Check the gases for correct pressure
- Check the eluent container for level
- Check the waste container for fluid level
- Open Chromeleon and start the instrument
- Prepare standards, if necessary
- Prepare sequence, with STOP at the end of the list
- Load samples

- Begin run
- Process the data
- Copy files to the proper data directory on EAFMAIN and complete the project status sheet

4.6 TROUBLESHOOTING

Use the Reference Library CD that is provided by DIONEX. The Technical Support Center (800-346-6390) has knowledgeable technicians, and the online help (callcenter@dionex.com) is quick to respond to questions.
Common problems and their solutions are:

Autosampler doesn't start with the start command. Verify that the AS40 is in the RUN mode (front panel).

The autosampler controls are set by default with the values: Type = Loop, Mode = Prop, Bleed = Off. Other lights are method controlled and cannot be selected.

The autosampler still doesn't start. The relay may be worn out. Change the program to use relay 2.

The valves do not switch. Check the air cylinder; the pressure must be above 100 psi.

There is a leak message on the menu screen. Check the valves on the GP50. Tighten the leaking nuts one-eighth of a turn at a time until the leaking stops. Dry the unit. It will reset itself.

The baseline is not stable. Check that the eluent reservoirs have eluent in them. If they are empty, prime the pump after filling the reservoir. There is a button on the panel face. Follow the directions.

Peak shapes are not sharp. The column may need to be replaced. Try cleaning it first.

Overlapping peaks. If the retention times have shifted too close to the water dip, the ions will elute and overlap. Try cleaning the column; otherwise, replace it.

High pump pressure. There may be blockage in the line. Trace the sample stream from the autosampler, disconnecting and replacing until the blockage is cleared.

Low Pump Pressure. This may be due to air in the line. Prime the pump. There is a **Prime** button on the panel face. Follow the directions.

Leakage from the ASRS. If the pump has been off, the membranes may dry out. Try running at low flow for a while; if it still leaks, replace it.

5.0 DATA COMPILATION AND FILE MANAGEMENT

5.1 Validation of the Chromatograms

Visually inspect every chromatogram to ensure that the samples have been collected properly, the peaks are identified correctly, there are no errors in the labels of the samples, the peaks are adequately drawn, and the areas are completely integrated.

- Proper Collection: A typical chromatogram is shown in Figure 5.1. The baseline should be constant before the water dip, return to its baseline position after the water dip and between components. A shifting or noisy baseline may indicate air bubbles in the line caused by leakage at the pump, air leaks affecting the conductivity cell, or running out of eluent.

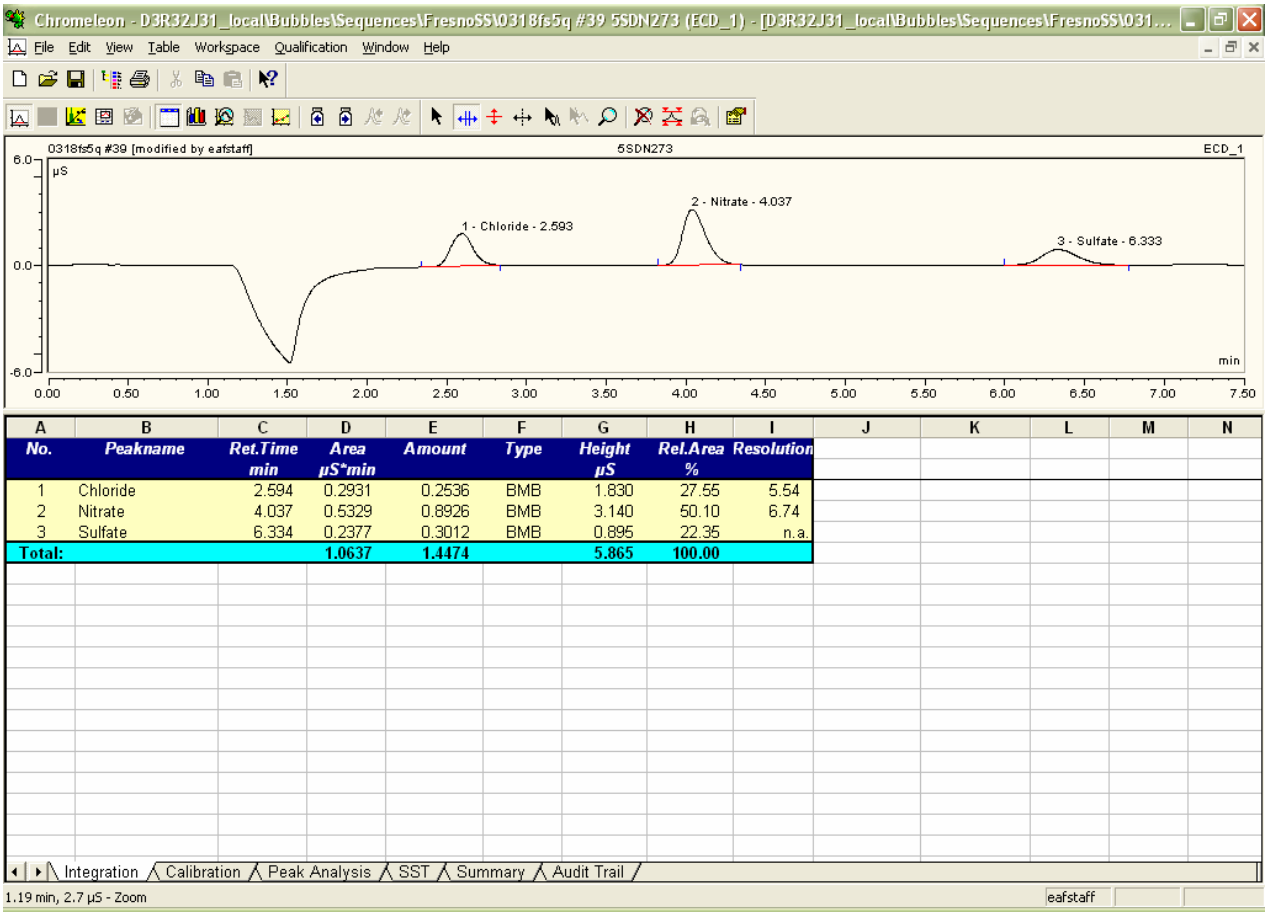
- Peak Identification: Occasionally, the constituents of a sample will be misidentified by the instrument due to a shift in the retention time during the run. This can be caused by very high concentrations, viscosity of the sample, or deterioration of the column. The peaks should be compared with the standard peaks and a determination made of the identity of the peaks from the comparison and the order of elution. If the components cannot be identified on that basis and if the concentrations seem very high, dilute and rerun the samples. Correct the identification in the .qnt Peak Table by changing the window size.

- Sample Peaks and Integration: Peaks should rise from the baseline and remerge smoothly with it. It is necessary to redraw the baselines if the drawn integration line does not look proper: it cuts off the peak prematurely or extends too far from the peak on the baseline (fronting or tailing). To reintegrate:

  Click the blue delimiter icon on the toolbar. Move the mouse along the baseline near the peak until the pointer changes its shape: an up-pointing marker indicates the peak start, while a down-pointing mark indicates the peak end. Left-click and drag the tool until the fronting is eliminated. After moving a peak delimiter, CHROMELEON draws a new baseline between the peak start and the peak end. Repeat on the tailing side if necessary. All peak properties such as area, width, substance amount etc. are recalculated. The integration report is immediately updated. Select the **Save Manipulations** command on the context or **Edit** menu to save the reprocessed results.

5.2 Calculation of Concentrations in the Extraction Solution

The peaks in the chromatograms are identified and area counts are converted to concentrations in mg/mL and printed on the chromatogram. An example of a typical ion chromatogram for ambient samples is illustrated in Figure 5-1. Any samples that have amounts above the highest standard in the calibration curve must be diluted and re-analyzed.



No.	Peakname	Ret.Time min	Area µS*min	Amount	Type	Height µS	Rel.Area %	Resolution
1	Chloride	2.594	0.2931	0.2536	BMB	1.830	27.55	5.54
2	Nitrate	4.037	0.5329	0.8926	BMB	3.140	50.10	6.74
3	Sulfate	6.334	0.2377	0.3012	BMB	0.895	22.35	n.a.
Total:			**1.0637**	**1.4474**		**5.865**	**100.00**	

Figure 5-1. Sample chromatogram.

5.3 Calculation of Concentrations on the Filter

When the analysis is complete, the sequence is batched to an Excel file, the file is manipulated so that the columns match the .dbf structure, then formatted and saved to a .dbf file, which .dbf is imported into the structure file and the calculation completed.

Batching the sequence

- Highlight the sequence to be batched. From the **File** dropdown menu, select **Batch Report.**
- In the next window, choose **report definition** "anion summary export", uncheck **printout** box , check **export** box.
- In the next window, select the **destination directory** in the top box using **browse**; delete the contents of **directory formula** in the middle box, in the bottom box save the file to the proper directory using the same filename as the sequence, check the box with the file format export as *.xls.
- In the next window, keep only the **summary** checkbox, uncheck the other boxes. Select **finish**, then *OK.*
- Answer "**Yes to All"** when asked about overwriting. The sequence will batch. Click **OK** at the end.

Converting from .xls to .dbf

- Open Excel and the proper *.xls file, which will be located in the directory that was chosen when the sequence was batched. (If this directory has escaped from memory, it can be found at the top of the printed sequence.)
- Using the data base structure as a guide, rename the columns: run id, qid, *species of interest,* dilf, anif, and date. Consult the analysis list for the species of interest. They may be any or all of the following Fliml, Climl, N2iml, Briml, N3iml, P4iml, and S4iml. Delete all columns and rows that are not requested on the analysis list.
- Highlight and format the cells with the species of interest in them to a number format with 4 decimal places. Using the replace icon, replace all n.a. with zero.
- Format the analysis date.
- Under page setup, identify the run with a custom header which contains the project name and filter type. Add gridlines for clarity when checking the data. Format the page to 1 page wide and whatever height is necessary. Print the sheet and check each over-range and zero value by reviewing the chromatogram.
- Save the file to a .dbf file in the Project Files directory with the same name as the sequence. Save the modified Excel file with filenamef.xls so that it can be accessed in case of questions (f = final). The original batch file will have the original .xls name.

Modifying the structure, appending files , calculating concentrations

- Open ANSTRU.dbf in the C: **Project Files** directory. Copy it to the directory that contains the .dbf file just created saving it to the name that is designated on the analysis

list. **Use** that file. In the command window, type "modi stru" and delete the species not needed.

- Append all of the runs appropriate to the analysis list, including any reruns and dilutions.
- **Do** program "ancal15", (or "antcal10", depending on the extraction volume), which will input QA flags, extraction volumes, and area factors.
- If there have been dilutions, index on id, replace the species with the appropriate value and mark the diluted record for dilution.
- **Do** 'anrecalc' to recalculate the concentrations whose iml values have changed.

Final checking of the database, calculation of precision, and disposition of the file

- Index on the individual fields to check:
    1. that all extraction volumes and area factors are correctly applied to the samples and the standards.
    2. that there are no major outliers in the concentration fields.
    3. that all of the samples on the analysis list were run.
- **Do** "Finddup" to verify that the only duplicate samples are replicates, blanks, and QA samples.
- **Do** "Setdef" to set the correct data directory. **Do** "Filter" and run the precision calculations.
- Copy the completed .dbf and its *.rep files to the assigned data directory on EAFMAIN.
- Post the date of completion in the Project Status Sheets.
-

5.4 Calculations

5.4.1. These steps should be followed if manual calculation of concentrations is necessary.

1. Determine the linear regression of the calibration curve for each ionic species. The calibration equation is given by the following relationship.

$$mg/mL = SLOPE\ (integrator\ reading) + intercept \qquad (5\text{-}1)$$

2. Calculate concentrations of sample extract corresponding to the area counts according to the calibration curve.

3. Calculate the total amount of ionic species in precipitation samples or in the filter by using the appropriate factors and record on the data sheet.

$$mg/filter = mg/mL \times V \times D \times F \qquad (5\text{-}2)$$

where:

V = volume of extract

D = dilution factor

F = scaling factor, determined by ratio of filter size to the fraction analyzed

5.4.2 Precision Estimates

Precisions reported in the data bases are propagated from the precision of the replicated analysis and the field blank variability using the methods of Bevington (1969). The following formulae describe the calculation of the precision propagation:

$$B_i = \frac{1}{n}\sum_{j=1}^{n} B_{ij} \qquad \text{for } B_i > \sigma_{B_i} \qquad (5\text{-}3)$$

$$B_i = 0 \qquad \text{for } B_i \le \sigma_{B_i} \qquad (5\text{-}4)$$

$$\sigma_{B_i} = STD_{B_i} = \left[\frac{1}{n}\sum_{j=1}^{n}\left(B_{ij} - B_i\right)^2\right]^{1/2} \qquad \text{for } STD_{B_i} > SIG_{B_i} \qquad (5\text{-}5)$$

$$\sigma_{B_i} = SIG_{B_i} = \left[\frac{1}{n}\sum_{j=1}^{n}\left(\sigma_{B_{ij}}\right)^2\right]^{1/2} \qquad \text{for } STD_{B_i} \le SIG_{B_i} \text{ and } B_i \ge SIG_{B_i} \qquad (5\text{-}6)$$

$$\sigma_{B_i} = 0 \qquad \text{for } B_i < SIG_{B_i} \qquad (5\text{-}7)$$

$$D_{M_{ij}} = M_{ijf} - M_{ijr} \qquad (5\text{-}8)$$

$$D_{M_i} = \frac{1}{n}\sum_{j=1}^{n} D_{M_{ij}} \qquad (5\text{-}9)$$

$$\sigma_{M_i} = \left[\frac{1}{n}\sum_{j=1}^{n}\left(D_{M_{ij}} - D_{M_i}\right)^2\right]^{1/2} \qquad (5\text{-}10)$$

where:

M_i = amount of species i on the substrate
M_{ijf} = amount of species i on sample j from routine analysis
M_{ijr} = amount of species i on sample j from replicate analysis
B_i = average amount of species i on field blanks
B_{ij} = the amount of species i found on field blank j
σ_{B_i} = blank precision for species j
σ_{M_i} = precision of amount of species i on substrate

6.0 QUALITY CONTROL

The quality control procedure serves two main purposes: 1) to identify possible problems with the measurement process, and 2) to calculate the precision of ion measurements.

6.1 Performance Testing

In addition to the daily start-up described in Section 4, the analysis sequence for standards, blanks and replicates should be followed as described in Section 4.3.2, resulting in approximately 10% standards check, 10% replicates and 5% blank checks.

6.2 Reproducibility Testing

Reproducibility is examined with the 10% replicate analyses during the routine sample analysis. The samples are extracted only once, so the replicate analysis refers only to the IC analysis of the extract. The precision of the replicate analysis will be calculated as stated in Section 5.4.2.

6.3 Tolerances and Actions to be Taken

Tolerances are generally ±30% at levels between 0.030 and 0.100 mg/mL; ±20% at levels between 0.100 and 0.150 mg/mL; and ±10% at levels above 0.150 mg/mL. If replicates exceed these tolerances, analyses beyond the last acceptable replicate are suspected to be incorrect. The replicate analysis on the same sample should be repeated again. If the second replicate duplicates, the original sample result, the first replicate result can be taken as spurious. Another replicate should be selected from samples within the same set of 10, after that first spurious replicate, and analyzed to verify that assumption. If the second replicate analysis exceeds the tolerance criteria, the cause of the error (probably in the instrument or the chemistry of the analysis) must be determined. Then, the whole set of 10 samples must be reanalyzed. Notify the laboratory supervisor immediately if sample rerun is to be performed.

6.4 Data Validation Feedback

The sample validation philosophy follows the three-level approach devised by Mueller et al., (1983) in the Sulfate Regional Experiment (SURE). Level I sample validation takes place in the field or laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred, 2) verifying computer file entries against data sheets, 3) eliminating values from measurements which are known to be invalid because of instrument malfunctions, 4) replacing data when re-analyses have been performed, and 5) adjusting measurement values for quantifiable calibration of interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master database. Level II applies consistency tests based on known physical relationships between these variables in the assembled data.

Level III sample validation is part of the data interpretation process and will be performed by each project manager and subsequent data users. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause.

The laboratory supervisor should review all the QC data as soon as it becomes available and ensure the feedback from the QC results to the routine operations. The project manager should consult with the QA officer to initiate and document changes to the data base as they are needed.

7.0 QUALITY ASSURANCE

Performance and system audits are scheduled for specific projects by the designated QA group on a project specific basis. As a general rule the EAF encourages inter-laboratory performance audits and participates when possible.

8.0 REFERENCES

ASTM, Annual Book of Standards, 1982

Bachman, S.R., J.E. Rothert, B. Kaiser, C.J. Brennan, and M.E. Peden (1986). Method 300.7 – Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography. Prepared for U.S. EPA, Cincinnati, OH by Illinois State Water Survey, Analytical Chemistry Unit, Champaign, IL.

Dionex Reference Library, CD, February, 2004.

Hidy, G.M., B.R. Appel, R.J. Charlson, W.E. Clark, D. Covert, S.K. Friedlander, R.D. Giauque, S.L. Heisler, W.W. Ho, J.J. Huntzicker, T. Novakov, L.W. Richards, R.C. Ragaini, T.B.

Smith, G.M. Sverdrup, S. Twiss, A.P. Waggoner, H.H. Wang, J.J. Wesolowski, K.T. Whitby, and W.H. White (1974). "Characterization of Aerosols in California (ACHEX) Vol. IV: Analysis and Interpretation of Data." Report for the California Air Resources Board Prepared by Rockwell International, Thousand Oaks, CA.

Mueller, P.K., G.M. Hidy, J.G. Watson, R.L. Baskett, K.K. Fung, R.C. Henry, T.F. Lavery, and K.K. Waren (1983). "The Sulfate Regional Experiment: Report of Findings, Volumes 1, 2, and 3." Report EA-1901, Electric Power Research Institute, Palo Alto, CA.

Small H., T.S. Stevens, and W.C. Bauman (1975). "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection." *Anal. Chem*., 47, 1801.

Watson, J.G., J.C. Chow, and J.J. Shah (1981). "Analysis of Inhalable and Fine Particulate Matter Measurements", Prepared for the U.S. EPA, EPA Report EPA-450/4-81-035.

Watson, J.G., P.J. Lioy, and P.K. Mueller (1983). "The Measurement Process: Precision, Accuracy and Validity." In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants* (6th Ed.), P.J. Lioy and M.J.Y. Lioy, eds. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, p. L-2

Watson, J.G., J.L. Bowen, J.C. Chow, R.T. Egami, A.W. Gertler, and K.K. Fung (1989). "Revised Program Plan for California Acid Deposition Monitoring Program." Document No. 8868.1D1, prepared for California Air Resources Board, Sacramento, CA, by Desert Research Institute, Reno, NV.

APPENDIX A.8

DRI STANDARD OPERATING PROCEDURES — Pages: 24

Date: 11/20/98

Title: Analysis of Filter Extracts and Precipitation Samples for Ammonium by Automated Colorimetric Analysis — Number: 2-207.5 — Revision: 5

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are to:

- provide a basic understanding of the principles of operating the Technicon Random Access Automated Colorimetric System (TRAACS) 800 Continuous Flow Analyzer,
- describe routine analysis of ammonium ion (NH_4^+) in aqueous filter extracts or precipitation samples using the Technicon TRAACS 800,
- detail the concerns and procedures which will insure a state-of-the-art measurement process.

This procedure will be followed by all analysts in the Environmental Analysis Facility (EAF) of the Energy and Environmental Engineering Center (EEEC) of the Desert Research Institute (DRI).

1.2 Measurement Principles

The measurement of ammonium ion in water and waste water by the Technicon TRAACS 800 is based on the Berthelot reaction (Berthelot, 1855). Indophenol blue, a blue dye, is formed when phenol and hypochlorite react with ammonium in an alkaline solution. Sodium nitroferricyanide is added to intensify the color.

The sample is drawn into the reaction coils by a peristaltic pump, mixed with alkaline phenol, sodium nitroferricyanide, sodium hypochlorite, and the disodium salt of ethylenediaminetetraacetic acid (EDTA), passed through a heated zone (37 °C for two minutes), and passed through a photocell detector. The absorbance at 660 nm is measured and converted to µg/ml. Brij-35 is added as a surfactant to the EDTA solution to aid in bubble formation. Bubbles are introduced into the sample tubing to aid in mixing the reagents and to serve as delimiters between samples.

1.3 Measurement Interferences and their Minimization

The presence of alkali metals in the sample will cause precipitates to form at high pH (high alkalinity). The resulting opacity will interfere with the colorimetric detection. The formation of these precipitates can be prevented by the addition of EDTA to the sample stream as a complexing agent.

Metals such as copper and aluminum can compete with the indophenol reaction, causing a decrease in sensitivity (Berthelot, 1855). The EDTA will complex with these metals also, decreasing the interference.

1.4 Ranges and Typical Values of Measurements

A wide range of ambient concentrations can be found in both filter extracts and precipitation samples. NH_4^+ concentrations ranged from 0 to 10 $\mu g/m^3$ in ambient samples from the Denver airshed (Watson et al, 1988) with a median value of 1 $\mu g/m^3$. The measurement range of this procedure is 0 to 3 µg/ml. Sample extraction and dilution parameters are adjusted so that sample concentrations fall in this range. In general, "typical" concentrations are difficult to express except in terms of ranges, because measured values, in µg/ml, depend on volume of extract or sample, amount of filter extracted, type of sample (i.e., urban or rural ambient, direct or diluted source), volume of air sampled, and filter deposit area.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The minimum instrumental detection limit of ammonium with the Technicon TRAACS 800 is 0.022 µg/ml based on the manufacturer's specifications, and confirmed by blank analyses. The precision and accuracy of the Technicon measurement of ammonium depends on the sample matrix and individual techniques. In general, the accuracy of the TRAACS 800 is dominated by the uncertainties in the standard solution preparation and is typically within ±10%. Precision as estimated by replicate analyses is in the range of better than ±10% for sample concentrations well above the detection limit to ±30%, for sample concentrations near the detection limit.

1.6 Responsibilities of Personnel

All analysts in the laboratory should read and understand the entire standard operating procedure and understand the operation of the Aace software before performing the ammonium analysis on the TRAACS 800. The analyst must follow the procedure for routine system calibrations, chemical analysis and performance tests.

It is the responsibility of the laboratory analyst to ensure that the colorimetric analysis procedures are properly followed, to examine all replicate, standard, and blank performance test data, to designate samples for re-analysis, and to deliver the analysis results to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible for determining the extent and methods of quality assurance to be applied to each project, for estimating the level of effort involved in this quality assurance, for identifying the appropriate personnel to perform these QA tasks, for updating this procedure periodically, and for assuring that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used in this document:

Berthelot Reaction: Berthelot first reported that a blue color is produced when phenol and hypochlorite react with ammonium in an alkaline reaction.

Bubble Pattern: Air is injected into the sample stream to aid in mixing and separating samples, allowing steeper concentration gradients by keeping the samples separate. The bubbles should be oblong, well separated, and present a repetitive pattern. A change in the bubble pattern is an indication of possible trouble.

Carryover Adjustment: In the analyzer tubing, samples can be contaminated by previous samples due to carryover. To calculate the amount of contamination, the protocol comment 'H,2L' will cause one high sample (usually the QA 2.00 mg/ml standard) to be analyzed and one low sample (usually DDW) to be analyzed twice. The difference between the two low analyses are then used to calculate the carryover. This correction is used in the final calculation of the data.

Detection Limit: Three times the standard deviation of a blank sample.

Gain Peak Number: The number of the sample peak used to correct for possible baseline drift in analytical response during an analysis run. A calibration standard used early in the run is reanalyzed periodically during the run and as the last sample in the run, and the gain is adjusted to minimize the difference in the responses. The sample used for gain adjustment must have a response of greater than 50% full scale.

Peristaltic Pump: The pump squeezes flexible small diameter tubing between a rotating set of rollers and a platen, causing the fluids to be pumped. Flow rates are governed by the interior diameter of the tubing.

Reaction Coils: Glass coils with 5 or 20 turns in which the different reagents mix to form the colorimetric reaction.

Photocell Detector: Flow cell through which a beam of light at a specific wavelength (660 nm) is passed. The difference in light absorbance due to the analyte is detected and converted to µg/ml.

Pump Tubing: The tubing used in the peristaltic pump to carry the liquids. These are color coded according to their inner diameters.

Tray Protocol: The commands which define the order in which the autosampler will access the sample cups. These commands include naming the type of sample in the cup, the number of times it will be analyzed, and its location on the auto sampler tray.

1.8 Related Procedures

Related procedures are specified in the following:

DRI SOP # 2-201.3 Sectioning of Filter Samples

DRI SOP # 2-202.3 Extraction of Ionic Species from Filter Samples

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The Technicon TRAACS 800 is an automated, continuous flow spectrophotometric instrument. It consists of the analytical console (peristaltic pump, reagent mixing coils, heating coil, and detector), a random access linear autosampler, an IBM compatible personal computer (PC), and a dot matrix printer (Figure 2-1).

An overall flow schematic appears in Figure 2-2. A schematic of sample flow through the colorimetric detector cell and of associated detector signal process is depicted in Figure 2-3.

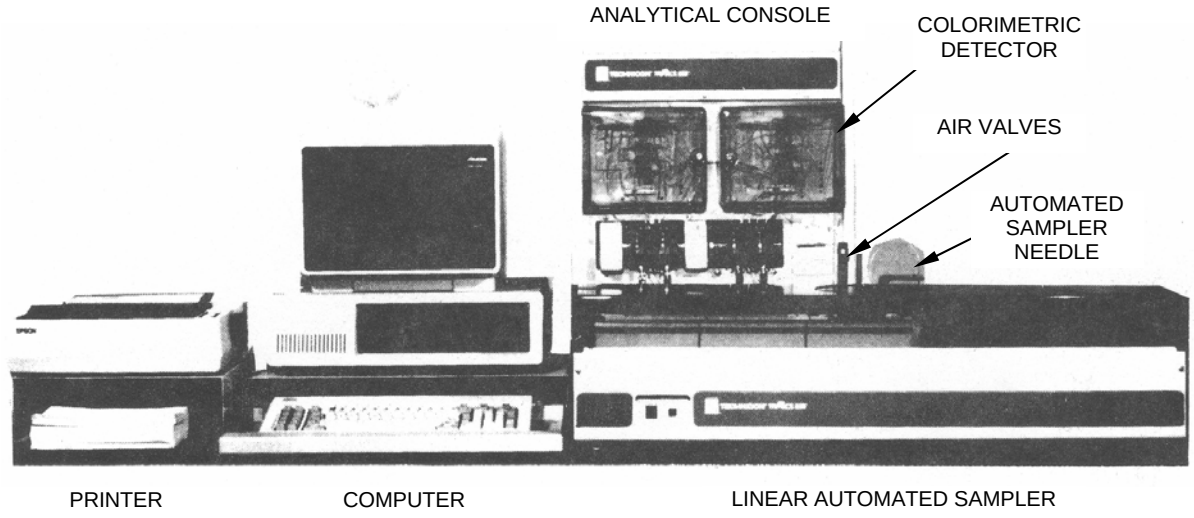


Figure 2-1. Technicon TRAACS 800 system overview.

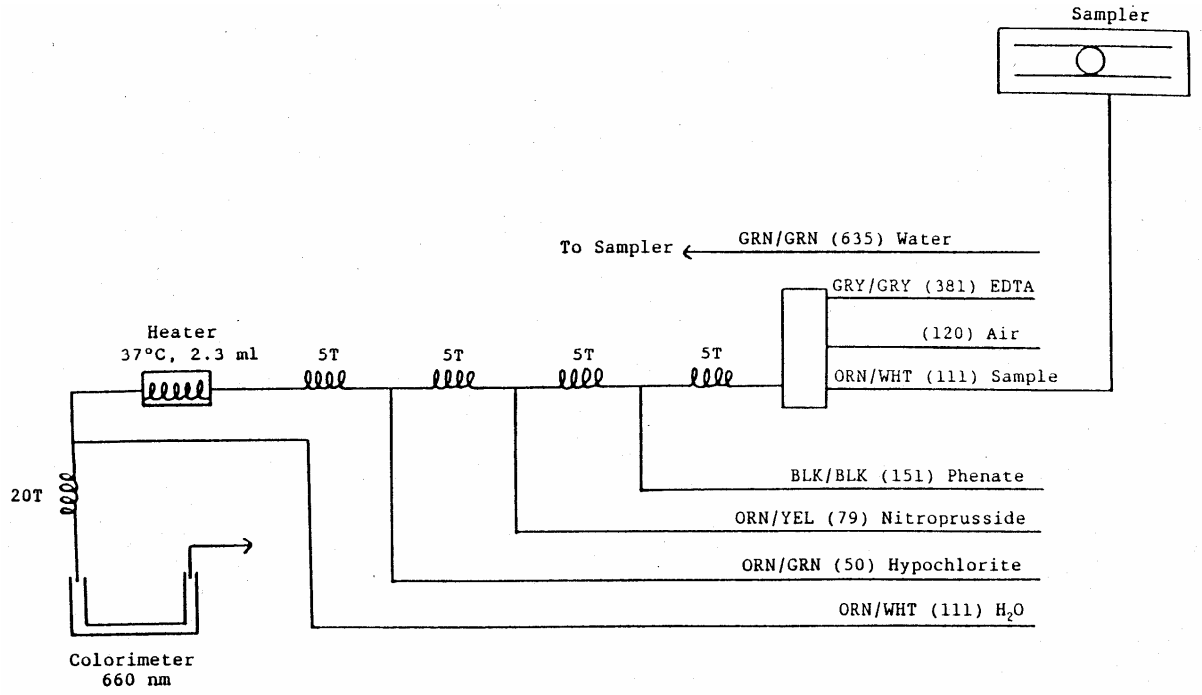


Figure 2-2. Technicon TRAACS 800 flow schematic.

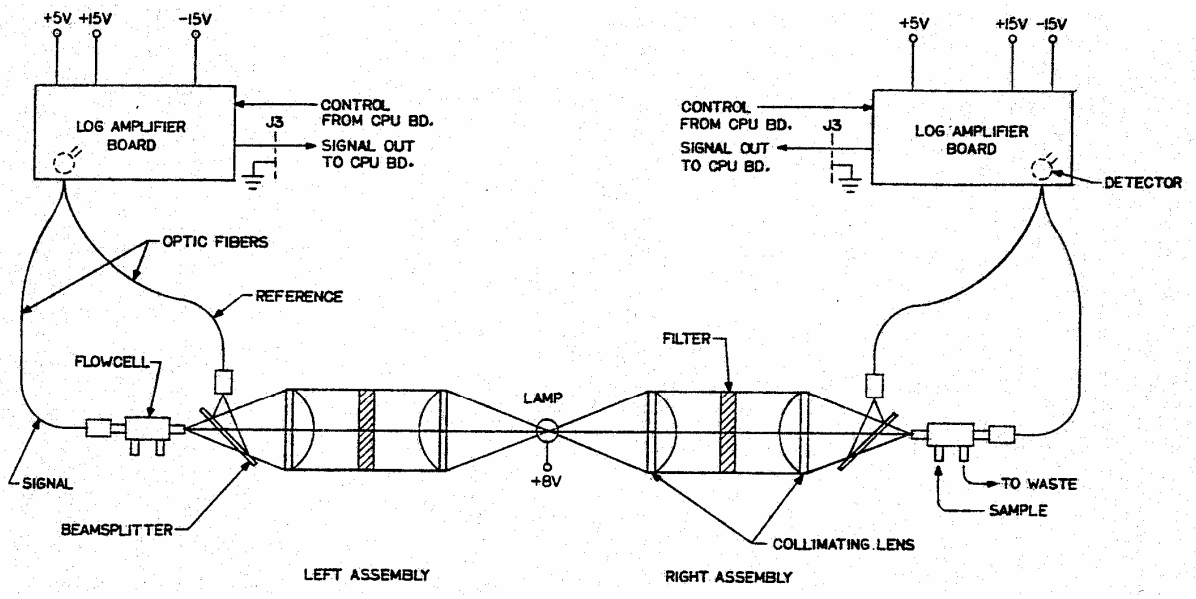


Figure 2-3. Technicon TRAACS 800 detector schematic.

The linear autosampler is a random access sampler, capable of accessing samples in any order specified, with sampling rates as high as 240 samples per hour. The autosampler provides positions for 120 4 ml polystyrene sample cups, as shown in Figure 2-4.

The Technicon TRAACS 800 instrument is controlled by the Aace computer program. The Aace software is a Windows 95 based program that provides full multitasking. It contols all aspects of the analyzer operation, including: TAACS control, reporting, quality control and data storage. This software controls the flow of the reagents, the base and gain of the photometric signal amplifier, the sampling interval, the type of sample, the order of the samples, the concentration of the standards, and the name of the samples. The software plots absorbences as the samples are analyzed (in a strip chart format), plots the calibration data, calculates the concentrations of the samples, and saves the data in both chart and text file formats on a hard disk. The text file is then transferred to a data base file and further manipulated to produce a report.

The software incorporates an extensive help library based on the operation manual. The Help feature is context sensitive, clicking the help button on any

window will take you directly to the help section for that window. Selecting the "Help" pulldown menu allows the analyst to search for information on specific operations or find troubleshooting information.

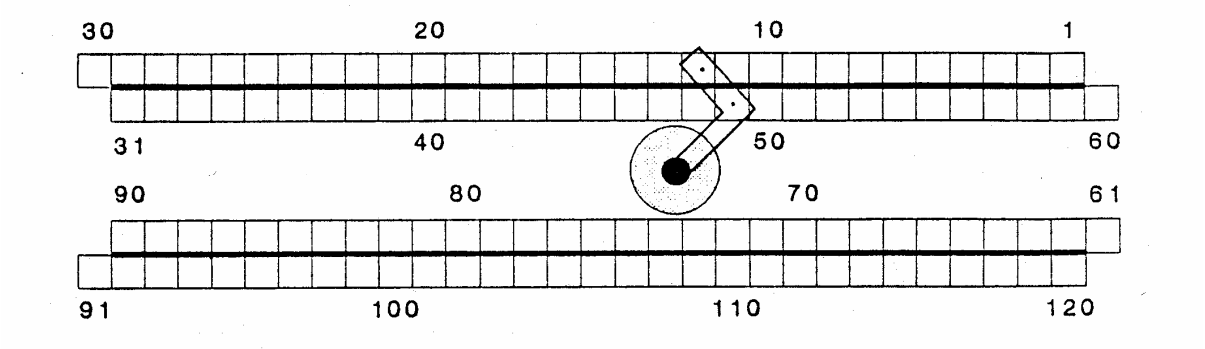


Figure 2-4. Technicon TRAACS 800 linear autosampler cup positions.

2.1.2 Instrument Characterization

The Technicon TRAACS 800 analyzes the contents of as many as 120 sample cups per run, including 8 standards, controls, 10% replicate samples, and 5% distilled-deionized water (DDW) blanks. One to two mL of each sample is placed in the 4 ml sample cups; replicates are sampled from different aliquots. The sampling rate is adjustable, but is currently set at 80 samples/hour.

The analyzer maintains a 2:1 ratio of sample volume to wash volume to reduce cross-sample interferences. The autosampler probe is rinsed between each sample at its home position. Transit time for a sample aliquot to travel from the sample cup to the colorimetric detector is approximately seven minutes.

The Aace program automatically establishes a nominal five percent baseline response at the beginning of each run and a baseline at the end of each run to characterize instrument stability.

The TRAACS 800 Analytical Console contains a dedicated microprocessor which operates on software downloaded from the PC. This program is lost whenever the Analytical Console is turned off or experiences a power failure. After such interruptions in electrical power, the program must be downloaded to allow the Analytical Console to operate properly (see Section 4.2).

CAUTION: THE PHENOLIC WASTES GENERATED BY THE COLORIMETRIC TECHNIQUE ARE HEALTH HAZARDS AND MUST BE HANDLED APPROPRIATELY. WASTE CONTAINERS SHOULD BE

CAPPED, CLEARLY LABELED, AND PROPERLY STORED WHEN FULL.

Additional information on health effects and proper handling procedures may be found in the Material Safety Data Sheets (MSDS) binder located in DRI's Environmental Analysis Laboratory or in the laboratory supervisor's office.

2.1.3 Maintenance

Regular maintenance of the TRAACS 800 includes the following:

- The peristaltic pump tubing has a rated lifetime of approximately 200 hours. This tubing should be replaced at least once per month under conditions of constant use. The tubing sections are color coded based on their inside diameters and consequently on their pumping capacities; tubing sections must be replaced with identically coded tubing. These tubing sections may also require replacing if bubble patterns change, extra bubbles appear, peak shapes are no longer flat on the top, or if the calculated carry over exceeds its normal range of 0.2 to 2.0%. Cut sample tube to $10^{3}/_{16}$ in. for proper ISAC phasing (pump to inlet manifold. See p. 3-42 of operation manual).

- The waste containers must be checked regularly and replaced when full. Refer to Section 2.1.2 for additional details.

- The analyzer should be cleaned every six months by sampling a 5 N sulfuric acid (H_2SO_4) solution for 30 to 60 minutes, followed by DDW for two to three hours.

- Printer paper should be checked before beginning each analysis run to insure a sufficient quantity is in place for the run.

- The printer ribbon should be checked and changed when the print quality changes from dark black to light black.

- The work areas should be kept clean.

- Additional maintenance and troubleshooting information may be found in the Technicon TRAACS 800 Operation Manual (Technicon, 1988), or by accessing the help feature of the Aace software.

2.1.4 Laboratory Supplies and Spare Parts

The following items must be kept in the laboratory to insure minimal interruptions to the colorimetric analysis:

- Compressed air supply: minimum of 28 liters/minutes flow rate a minimum pressure of 40 psi. DRI's building air supply is used after it has passed through an oil trap, a particulate filter, and a regulator set at 60 psi.

- Volumetric flasks: glass, 100.0 ml, Class A (±0.01 % accuracy)

- Pipettes: volumetric in 1, 2, 3, 5, 10, and graduated 5 ml sizes, Class A

- Sample cups: polystyrene, conical bottom, 4 ml capacity

- Peristaltic pump tubing:

941 ul/min tubing, GRN/GRN (Technicon, #178-3748P14)
568 ul/min tubing, GRY/GRY (Technicon, #178-3748P11)
166 ul/min tubing, ORN/WHT (Technicon, #178-3748P06)
226 ul/min tubing, BLK/BLK (Technicon, #178-3748P07)
118 ul/min tubing, ORN/YEL (Technicon, #178-3748P05)
74 ul/min tubing, ORN/GRN (Technicon, #178-3748P04)

- Printer ribbons

- Printer paper

2.2 Reagents

2.2.1 Use analytical grade chemicals for all solutions.

Use DDW conforming to ASTM specification D1193-91, Type I (Annual Book of ASTM Standards, 1996).

Ammonium sulfate: $(NH_4)_2SO_4$, reagent grade. Used for primary standard.

Brij-35, 30% solution: (P/N T21-0110, Technicon, Tarrytown, NY, Phone 914-333-6142). A surfactant.

Chloroform: $CHCl_3$ UV grade . Used as a preservative for the primary standard solution.

EDTA, disodium salt: disodium salt of ethylenediaminetetraacetic acid, $Na_2C_{10}H_{14}O_8N_2 \times 2H_2O$. Used as a complexing agent for interferences from metals.

Phenol, crystalline: C_6H_5OH, Reagent grade . Used to produce the colored complex with ammonia and hypochlorite.

Sodium hypochlorite: NaOCl, 5% aqueous solution, reagent grade. Used to produce the colored complex with ammonia and phenol.

Sodium hydroxide, 50% w/w solution: NaOH, reagent grade. Used to make phenol solution alkaline.

Sodium nitroferricyanide:, $Na_2Fe(CN)_5NO \times 2H_2O$, Reagent grade, . Used to enhance the blue color of the ammonia/phenol/hypochlorite complex.

Sodium Citrate: $Na_3C_6H_5O_7 \times 2H_2O$, reagent grade, . Used in filter extraction of citric acid impregnated filters and in matrix matching of standards.

Citric acid: $C_6H_8O_7 \times H_2O$, reagent grade, . Used in impregnating filters and matrix matching of standards.

Glycerol: $HOCH_2CHOHCH_2OH$, anhydrous, reagent grade . Used in impregnating filters and matrix matching of standards.

2.2.2 Preparation of Solutions

When solutions are prepared, label the container with the contents, concentration, date prepared, and analyst's initials.

Alkaline Phenol: Weigh 42.0 g of crystalline phenol (to the nearest 0.1 g.) into a disposable weighing boat. Transfer the chemical quantitatively to a 500 ml volumetric flask containing approximately 200 ml DDW by rinsing it into the flask with DDW from a wash bottle. Weigh 72.0 g of 50% w/w sodium hydroxide solution (to the nearest 0.1 g.) into a disposable weighing boat, and add very slowly to the phenol solution, with swirling. Rinse the boat used for the NaOH with DDW from a wash bottle to ensure complete transferal. Cool under running tap water or in an ice bath if necessary. After the solution cools, dilute to the mark with DDW. Transfer to a dark plastic bottle, store in the refrigerator. The solution is stable for about one month. CAUTION: BOTH INGREDIENTS ARE CORROSIVE. Wash with copious amounts of water if either contacts the skin. Clean bench area carefully after making this solution.

- Sodium hypochlorite solution: Use as is from reagent container. Pour into smaller 125 ml bottle which is labeled for such use.

- Sodium nitroferricyanide solution Weigh 0.55 g of sodium nitroferricyanide (to the nearest 0.01 g.). Transfer the chemical quantitatively to a 500 ml volumetric flask by rinsing it into the flask with DDW from a wash bottle and bring to volume with DDW and dissolve completely. Store in amber container in refrigerator. Stable for one month.

- EDTA solution: Weigh out 41.0 g of disodium EDTA (to the nearest 0.1 g.). Transfer the chemical quantitatively to a 1000 ml volumetric flask containing approximately 800 ml DDW by rinsing it into the flask with DDW from a wash bottle. Dissolve the EDTA (using stir plate) completely, weigh 1.0 g sodium hydroxide (50% w/w) solution into a disposable weigh boat. Transfer quantitatively to the volumetric flask containing the EDTA by rinsing it into the flask with DDW from a wash bottle, and then bring to volume with DDW. Add 3 ml Brij-35 and carefully mix Stable about six months. Note: the Brij-35 causes severe foaming when agitated.

- Wash for Citric Acid samples: Weigh 29.4 g of Sodium Citrate (to the nearest 0.1 g) and transfrer quantitatively to a 1000 ml volumetric flask containing approximately 800 ml DDW, disolve Sodium Citrate. Pipette 20 ml of 25% Citric Acid/5% Glycerol solution (as used to prepare Citric Acid standards) into the flask and bring to volume with DDW.

2.3 Forms and Paperwork

A sample analysis list will be prepared by the laboratory manager indicating which samples will be analyzed and any special instructions (Figure 2-6). Non-routine maintenance operations should be logged into the TRAACS Logbook.

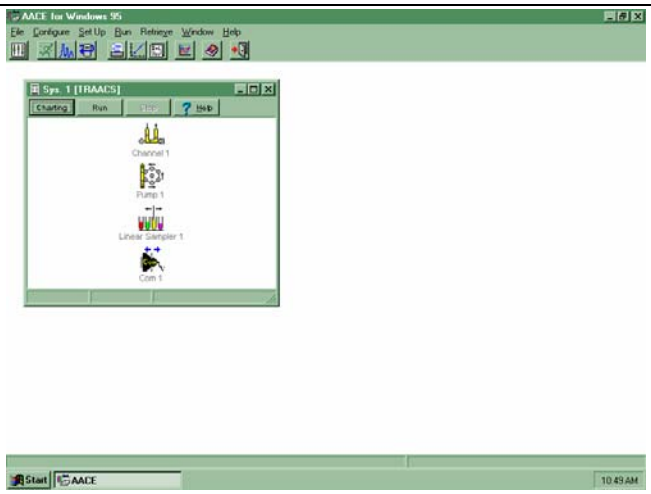


Figure 2-5. Technicon AACE software: Main Menu.

Menubar with AACE Main Menu

The AACE Main Menu provides the following menu options:

File	to select the printer, export data and exit AACE. See The File Menu.
Configure	to enter the configuration of your analyzing system and to choose software options. See The Configure Menu.
Set Up	to prepare analyses and runs as well as Quality Control charts. See The Set Up Menu.
Run	to adjust baseline and sensitivity, to start and stop runs, and to recalculate run results. See The Run Menu.
Retrieve	to access reports, charts etc. after a run. See The Retrieve Menu.
Windows	to change the arrangement of the windows on the desktop.
Help	to access context-sensitive on-line help.

The menu structure is as follows:

File	Configure	Set up	Run	Retrieve	Help
Select Printer	CFA System	Analysis	Chart	View Chart	Contents
Export To ASCII File	Software	QC Chart	Start	Print Chart	About
Logbook		Start up	Stop	Calibration Curve	
Exit		Shut down	Quick Start	Report	
		Reagent Seq.	Start up	Raw Data	
			Shut down	QC Chart	
			Recalculate		

See also:

Toolbar
System Windows
The AACE Main Menu Screen

Figure 2-6. AACE main menu options.

Toolbar

The tool buttons in the Toolbar are shortcuts for the following menu options:

- Set Up: Analysis (see Setting Up Analyses and Runs).
- Run: Quick Start (see Starting a Run Using Run - Quick Start).
- Retrieve: View Chart (see Retrieving a Chart).
- Run: Recalculate (see Recalculating a Run).
- Retrieve: Print Chart (see Printing a Chart).
- Retrieve: Calibration Curve (see Retrieving a Calibration Curve).
- Retrieve: Report (see Retrieving a Report).
- Retrieve: QC Chart (see Retrieving a QC Chart).
- Help Contents
- Exit (see Exiting AACE and Switching Off the Computer).

See also:

Menubar with AACE Main Menu
System Windows
The AACE Main Menu Screen

Figure 2-7. AACE toolbar description.

Weirton.94 Resuspension: Batch 03 Quartz

Date : 02/07/94

From: B. Hinsvark

To : S.Chandra
J.Chow
F.Divita
C.Frazier
G.Hargrove
J.Watson
Carbon Lab

Analysis: OC/ECby TOR : 20 samples, data in WROET03R.DBF
Cl-/N03-/S04= by IC : 20 samples, data in WRANI03R.DBF
NH4+ by AC : 20 samples, data in WRN4C03R.DBF
Na+ by AA : 20 samples, data in WRNAA03R.DBF
Mg++ by AA : 20 samples, data in WRMGA03R.DBF

Sample Overview:

This analysis list covers samples from the SAIC CMB, SIP project. These are 20 PM2.5 & PM10 samples on 47 mm Quartz filters, including no lab blanks and no field blanks. These samples were collected with a Resuspension sampler. This is the last batch for Weirton. It is the resuspensions.

Analysis Overview:

Sample deposit area: 13.8 cm2
Analysis start date: 2/7/94
Analysis deadline : 02/11/94
Sample location : CB2

Analysis Details:

Sample extractions must be scheduled with Wet Chem Lab personnel. Samples will be quantitatively halved and extracted in 15.0 ml DDW. Samples will be sonicated

for 60 minutes, shaken for 60 minutes, and left in the refrigerator overnight before analysis begins. Analysis data will be stored in the \WEIRTON.94 directory.

Carbon analysis data will be stored in the D:\WEIRTON.94\BATCH03 directory.

Figure 2-8. Example of DRI TRAACS analysis list.

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

The stock standard solutions should either be purchased as certified solutions or prepared from ACS reagent grade materials. These solutions should be properly labeled with the name of the chemical, concentration, initials of the analyst making it, and the date it was made.

3.1.1 Stock Standard Solution (SS), 100 mg/ml (as $NH4^{+}$):

The standard stock solution is prepared from ACS reagent grade ammonium sulfate [$(NH_4)_2SO_4$]. Weigh out 0.3667g ammonium sulfate (to the nearest 0.0001 g) into a disposable weighing boat. Transfer quantitatively to a 1000 ml glass volumetric flask by rinsing it into the flask with DDW.

From a wash bottle, add 1.0 ml chloroform as a preservative and bring to volume with DDW. Mix thoroughly. The final concentration of ammonium ion is 100.0 mg/ml. Store in refrigerator. This solution is stable for one month without a chloroform preservative, and stable for about one year with chloroform.

3.1.2 Working Standard (WS), 10 mg/ml:

This is an intermediate standard solution used for the preparation of calibration standards. Pipette 10 ml (using a Class A pipette) of Standard Stock Solution into a 100.00 ml glass volumetric flask and bring to volume with DDW. Mix thoroughly. The final concentration is 10.00 mg/ml. Store in refrigerator. This WS is stable for one month.

3.1.3 Calibration Standards for routine ammonium analysis:

Prepare calibration standards in concentrations of 0.050, 0.100, 0.300, 0.500, 1.000, 2.000 and 3.000 mg/ml. Use 100.00 ml glass volumetric flasks, and store in refrigerator. These may be used for one month.

0.050 mg/ml: Pipette 0.500 ml (using a Class A graduated pipette) of the 10.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

0.100 mg/ml: Pipette 1.000 ml (using a Class A pipette) of the 10.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

0.300 mg/ml: Pipette 3.00 ml (using a Class A pipette) of the 10.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

0.500 mg/ml: Pipette 5.00 ml (using a Class A pipette) of the 10.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

1.000 mg/ml: Pipette 10.00 ml (using a Class A pipette) of the 10.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

2.000 mg/ml: Pipette 2.00 ml (using a Class A pipette) of the 100.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

3.000 mg/ml: Pipette 3.00 ml (using a Class A pipette) of the 100.00 mg/ml WS into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

ERA Reference Standards:

A single component calibration standard 100 µg/ml ammonium as NH_4^+ is used as a quality control check. This is diluted as follows:

Intermediate 10 µg/ml Standard: Pipette 10 ml (using a Class A pipette) of stock ERA reference standard into a 100 ml volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

2.00 mg/ml: Pipette 2.00 ml (using a Class A pipette) of stock ERA reference standard into a 100 ml volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

0.100 mg/ml: Pipette 1.0 ml (using a class A pipette) of the intermediate 10 µg/ml ERA standard into a 100.00 ml volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

3.1.4 Calibration Standards for filters impregnated with citric acid.

Prepare calibration standards in concentrations of 0.050, 0.100, 0.300, 0.500, 1.000, 2.000 and 3.000 mg/ml. Use 100.00 ml glass volumetric flasks and store in refrigerator. These may be used for two weeks.

Match the standard matrix solutions with the sample matrix by adding 10.00 ml 1M sodium citrate stock and 2 ml 25% citric acid/5% glycerol stock to each 100.00 ml flask. Prepare a blank in addition to the standards.

1 M Sodium Citrate Stock Solution: Weigh 29.4 g of sodium citrate (to the nearest 0.1 g.) into a disposable weighing boat. Transfer the chemical quantitatively to a 100 ml volumetric flask containing about 50 ml DDW by rinsing it into the flask with DDW from a wash bottle. Dissolve completely. Bring to volume with DDW. Store at room temperature.

25% Citric Acid/5% Glycerol Stock Solution: weigh 25.0 g citric acid (to the nearest 0.1 g.) into a disposable weighing boat. Transfer the chemical quantitatively to a 100 ml volumetric flask containing about 80 ml DDW by rinsing it into the flask with DDW from a wash bottle. Weigh 5.00 g glycerol into a weigh boat and transfer quantitatively to the 100 ml volumetric flask by rinsing with DDW from a wash bottle. Bring to volume with DDW. Mix thoroughly and store at room temperature.

Prepare standards as in Section 3.1.3.

3.2 Use

An additional audit check is made using one of the other commercially available standards or standard reference materials. Presently, Environmental Resource Associates Calibration and WasteWatR ^{TM} quality control standards are used.

ERA Nutrients WasteWatR is used as a quality control check for ammonia. The stock has a concentration of approximately 10µg/ml ammonia as NH_4^+. Dilute this 1:10 to get the concentration in range for the instrument by pipetting 10.00 ml (using a Class A pipette) of the ERA stock into a 100.00 ml glass volumetric flask. Bring to volume with DDW. Mix thoroughly. Store in refrigerator.

For the analysis of samples from citric acid impregnated filters, the matrix must be adjusted to match the matrix of the samples and standards. This requires the addition of sodium citrate (1 M) and 25% citric acid/5% glycerol to each QA standard. The matrix of the standards, controls, and wash must be matched for other sample types (e.g 0.2% Ethanol or Sulfuric acid) as well.

The laboratory analyst verifies the QA standards daily as a first level of validation. The working standards as well as selected calibration standards are prepared and analyzed by the laboratory manager or an external quality assurance auditor quarterly as an independent check. All working standards are kept in the laboratory as back up tracers until the data have been properly examined and reported.

3.3 Accuracy of Calibration Standards

The accuracy of calibration standards is primarily limited by variations in standard solution preparation and is typically within 10% of the nominal standard concentrations.

4.0 PROCEDURES

Routine analysis involves establishing a baseline with the reagents, analyzing standards to check if they produce a linear and reproducible instrument response, analyzing the standards and samples in the analysis run, and rinsing the system with water before shutting down.

4.1 General Flow Diagram

The typical flow of samples and data for TRAACS 800 analysis is depicted in Figure 4-1.

4.2 Instrument Start-Up

1. Turn on the main console, sampler, and computer.

2. Double click the Aace icon on the desk top to start the analysis program.

3. Allow the system to warm up for 20-30 minutes.

4. Fill the wash bottle with fresh DDW, connect the pump tubes by stretching them across the pump rollers to the lower holder and insert the colored clip into the holder. Insure that the tubes do not cross each other. Close

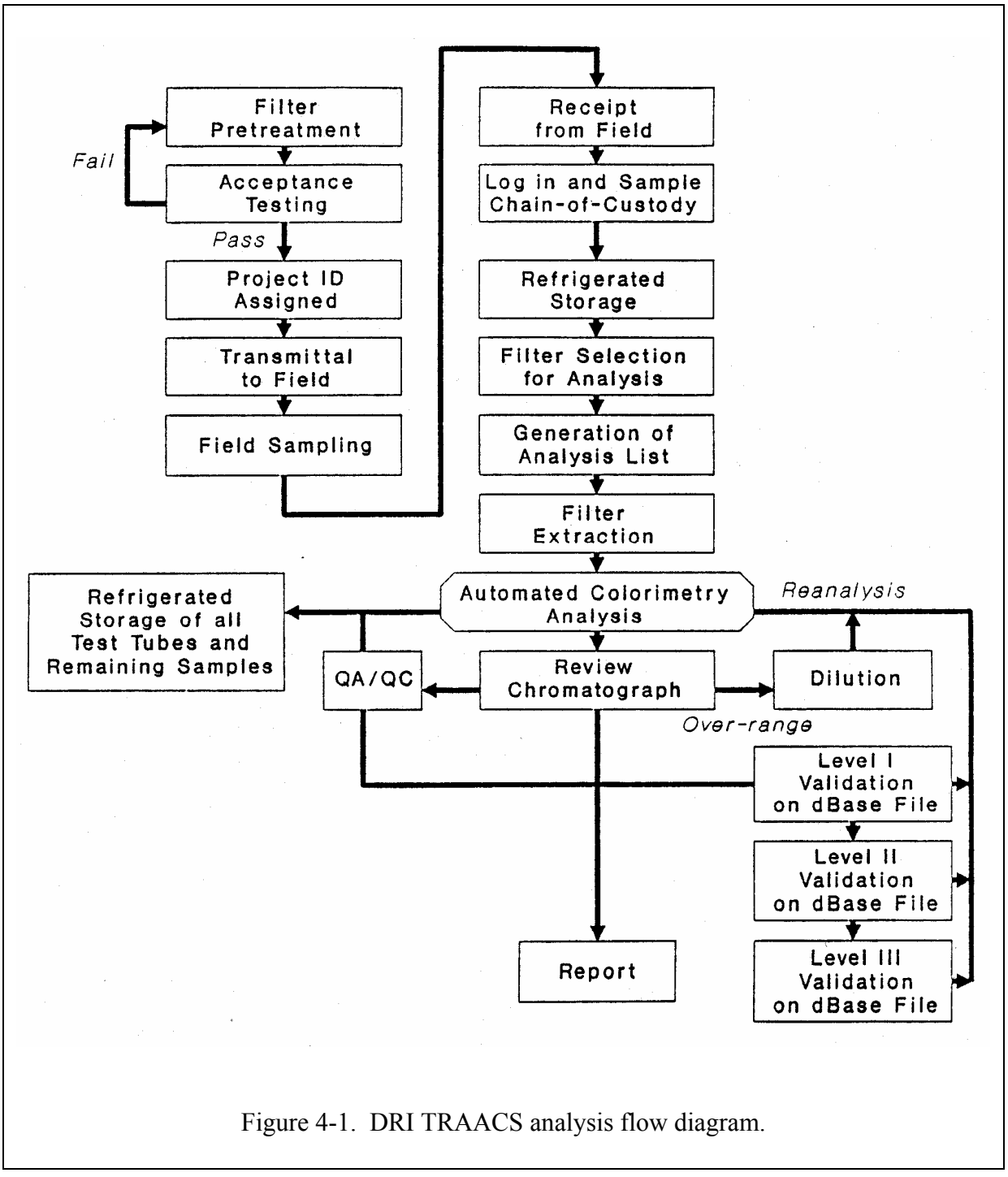


Figure 4-1. DRI TRAACS analysis flow diagram.

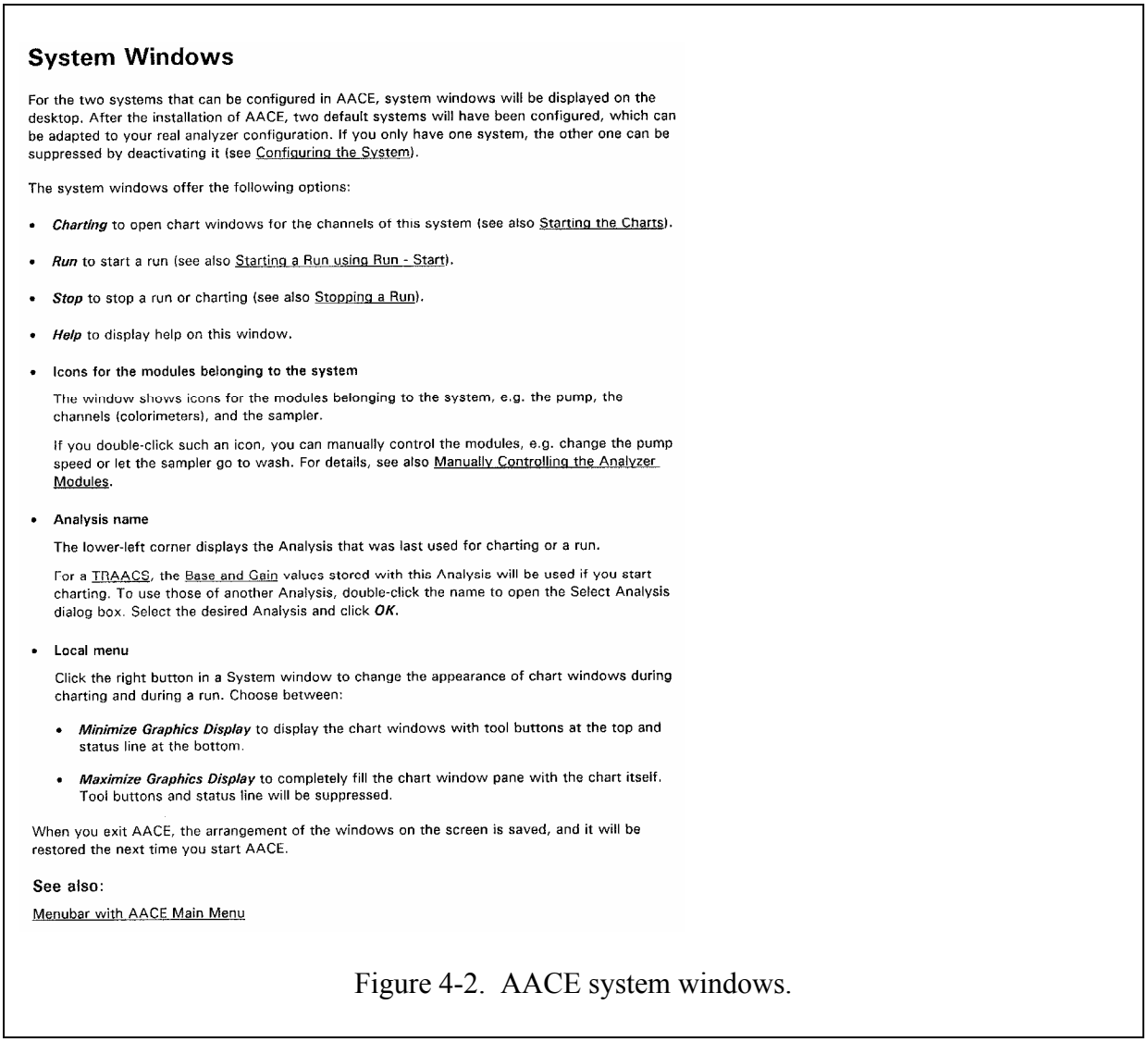
the platten by pushing it down and raising the black clips located at the bottom of the pump. Place them in the DDI wash solution.

5. Click the “CHARTING” button on the “System 1 [TRAACS]” window, (restore if necessary) or select the “Run” pulldown menu and select “Chart”. See Figure 2-5. If the power has been switched off or interupted during a run, it will be necessary to download the Aace program commands to the main console. The software will alert you to this fact. When the “Error” window appears, open the side door of the main console and press the red reset button (instead of switching the unit off and on as directed). Click “OK”. The pump will start and the software will begin charting when the download is complete.

6. Allow the system to pump water for ~15 minutes or until a stable bubble pattern is established.

7. Place the reagent lines in their respective reagent containers and allow to pump reagents until a stable baseline is established. This will take ~20 minutes.

Use the wash solution for Citric Acid samples when running Citric Acid impregnated filters, or other appropriately matrix matched wash (e.g.,



System Windows

For the two systems that can be configured in AACE, system windows will be displayed on the desktop. After the installation of AACE, two default systems will have been configured, which can be adapted to your real analyzer configuration. If you only have one system, the other one can be suppressed by deactivating it (see Configuring the System).

The system windows offer the following options:

- ***Charting*** to open chart windows for the channels of this system (see also Starting the Charts).
- ***Run*** to start a run (see also Starting a Run using Run - Start).
- ***Stop*** to stop a run or charting (see also Stopping a Run).
- ***Help*** to display help on this window.
- **Icons for the modules belonging to the system**

  The window shows icons for the modules belonging to the system, e.g. the pump, the channels (colorimeters), and the sampler.

  If you double-click such an icon, you can manually control the modules, e.g. change the pump speed or let the sampler go to wash. For details, see also Manually Controlling the Analyzer Modules.
- **Analysis name**

  The lower-left corner displays the Analysis that was last used for charting or a run.

  For a TRAACS, the Base and Gain values stored with this Analysis will be used if you start charting. To use those of another Analysis, double-click the name to open the Select Analysis dialog box. Select the desired Analysis and click ***OK***.
- **Local menu**

  Click the right button in a System window to change the appearance of chart windows during charting and during a run. Choose between:

  - ***Minimize Graphics Display*** to display the chart windows with tool buttons at the top and status line at the bottom.
  - ***Maximize Graphics Display*** to completely fill the chart window pane with the chart itself. Tool buttons and status line will be suppressed.

When you exit AACE, the arrangement of the windows on the screen is saved, and it will be restored the next time you start AACE.

See also:

Menubar with AACE Main Menu

Figure 4-2. AACE system windows.

0.2% EtOH or 0.1N H_2SO4.)

EDTA	Grey/Grey (568 ul/min)
Phenate	Black/Black (226 ul/min)
	(Note that the sample tube which goes to the sampler is also black/black.)
Nitroferricyanide	Orange/Yellow (118 ul/min)
Hypochlorite	Orange/Green (74 ul/min)
DDW/Citric Acid Wash	Orange/White (166 ul/min)
DDW/Citric Acid Wash	Green/Green (941 ul/min)

4.3 SETTING BASE & GAIN

It is necessary to check and, if required, set the base and gain values when new reagents or standards are made, or if the baseline is abnormally high or low. Base and Gain settings should not be changed until the system has been pumping reagents for ~ 20 minutes and the system is displaying a stable reading. Variations of less than +/- 5% need not be corrected manually. The software is configured to automatically set the baseline to a target value of 5%. Variations greater than 5% from the target value should be investigated. Abnormal baseline values may be due to old reagents or placing reagent lines in the wrong containers. Abnormal gain values usually result from old reagents or pouring the wrong standard.

1. Pour the 3.0 standard into a sample cup (nearly full) and place in the #1 cup position on the auto sampler.

2. Open the Channel 1 icon in the System 1 [TRAACS] window by double clicking it. A dialog box for adjusting the Base and Gain will appear.

3. Adjust the base value to ~5% by entering a new value or by clicking the arrows to increment the value.

4. Click "OK" to accept the value.

5. Open the Linear Sampler 1 icon.

6. Click "Sample" to send the probe to position 1. Sample for ~5 minutes.

7. Click "Wash" to return the probe to the wash receptical.

8. Click "Cancel" to close the Sampler window.

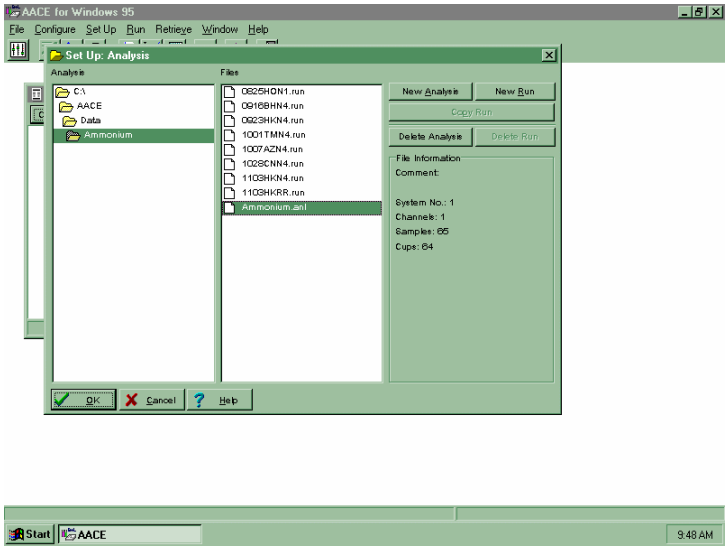


Figure 4-3. Selecting file to create a new run.

9. Wait for the standard to reach the detection cell (~8 minutes from the beginning of sampling) and reach a constant response.

10. Open the Channel 1 icon.

11. Adjust the gain value to achieve a response value of ~90%.

12. Allow the system to return to a stable baseline. Readjust to a value of ~5% if necessary.

13. Click “OK” to accept the values.

4.4 RUN SET-UP

A run may be set-up anytime, but is typically done while waiting for a stable reagent baseline. Additional information about any aspect of setting up the run or operation of the software can be obtained by accessing the “HELP” feature of the Aace software.

1. Select “SetUp” from the pulldown menus or click the Setup: Analysis button (first on left).

2. Select “Analysis” from the menu.

3. Double click the “Ammonium” folder (Figure 4-3).

4. Click the “Ammonium.anl” file to select it.

5. Click the “New Run” button.

6. Enter the run name in the format: MMDDPRN4, where; MM = month, DD = day, and PR = project code (Figure 4-4).

7. Enter a project description, typically the project and batch number.

8. Click the “Tray Protocol” tab.

9. Scroll down the protocol until the first block of blank sample cells is visible; peak #28, cup #12 (Figure 4-5).

10. Enter the sample IDs (and dilution factor if required) using the keyboard or light pen. Use the “down arrow” key to move down the list. The samples are entered in blocks of 11; 10 samples and 1 replicate. The protocol is setup for a standard run of 40 samples. It may be modified by adding or deleting samples as required.

11. Click the “printer” icon.

12. Click the “printer” icon on the preview page to print a copy of the protocol to be used as a loading guide.

13. Click “EXIT” to return to the tray protocol window.

14. Click the “OK” button to save the run.

15. Load the standards, controls, and samples onto the autosampler by pouring 1-2 mL into a sample cup and placing it into the position indicated on the tray report. Note that the standards and ERA controls will be sampled from the same cup for subsequent analysis. If samples are deleted, cups following the deletions will maintain their original positions(Figure4-6).

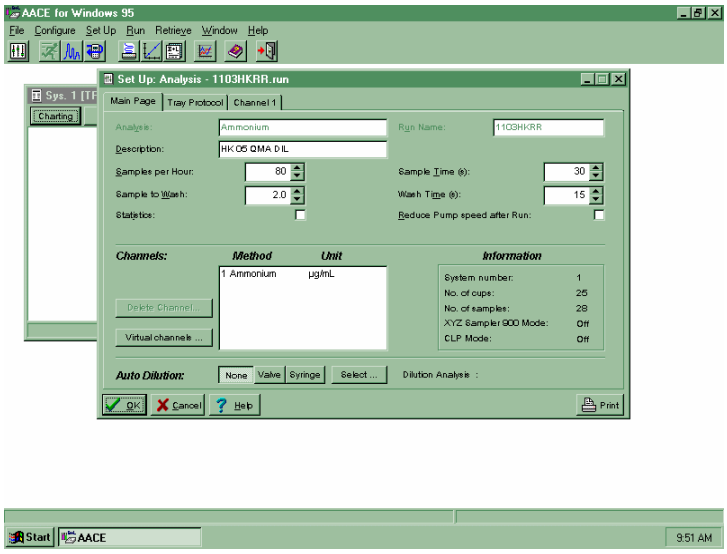


Figure 4-4. Entering run name and description.

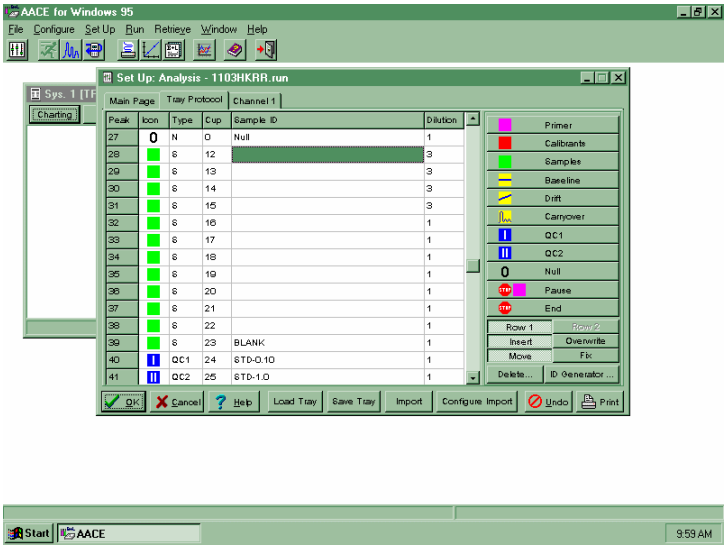


Figure 4-5. Entering sample IDs and dilution factors.

Name of Run	:1103HKRR	Name of Analysis	:Ammonium
Date	:11/5/98	System No.	:1
Sample/Hour	:80	Sample Time	:30
Sample/Wash	:2.0	Wash Time	:15.0
Statistics	:No	CLP	:No

Channel / Method

Channel	1
Method	Ammonium
Unit	µg/mL
Inverse Chem.	No
Sample limit	Yes
Sample limit low	0.0000
Sample limit high	3.3000
Base Correction	Yes
Drift Correction	Yes
Carry Over Corr.	Yes
Calibration Fit	Q
Base Calibration	No
Base Concentration	0.0000
Carry Over Factor	0.0000
QCLink	
QCCopy	No
Calibrant 1	3.0000
Calibrant 2	2.0000
Calibrant 3	1.0000
Calibrant 4	0.5000
Calibrant 5	0.3000
Calibrant 6	0.1000
Calibrant 7	0.0500
Calibrant 8	0.0000
Calibrant 9	0.0000
Calibrant 10	0.0000

QC Limits

QC1	cond. 1	Below
	limit 1	0.0800
	cond. 2	Above
	limit 2	0.1200
QC2	cond. 1	Below
	limit 1	0.9000
	cond. 2	Above
	limit 2	1.1000

Page 1

Tray / Cups

Number of Cups : 25 Number of Samples : 28

No	Cup	Type	Sample Id	Dilution
1	2	P	Primer	1
2	2	D	Drift	1
3	1	H1	High	1
4	0	L1	Low	1
5	0	L1	Low	1
6	1	CC	3.0	1
7	1	CC	3.0	1
8	2	CC	2.0	1
9	2	CC	2.0	1
10	3	CC	1.0	1
11	3	CC	1.0	1
12	4	CC	0.5	1
13	4	CC	0.5	1
14	5	CC	0.3	1
15	5	CC	0.3	1
16	6	CC	0.1	1
17	6	CC	0.1	1
18	7	CC	0.05	1
19	7	CC	0.05	1
20	8	CC	0.00	1
21	8	CC	0.00	1
22	0	N	Null	1
23	7	S	STD-0.05	1
24	9	S	ERA 0.1	1
25	10	S	ERA Nutrient	1
26	11	S	ERA 2.0	1
27	0	N	Null	1
28	12	S	TWFQ0017	3
29	13	S	TWRQ0017	3
30	14	S	TWFQ0018	3
31	15	S	TWRQ0018	3
32	16	S	TWFQ0019RR	1
33	17	S	TWFQ0011R	1
34	18	S	TWFQ0015R	1
35	19	S	TWFQ0020R	1
36	20	S	BLANK	1
37	21	S	BLANK	1
38	22	S	BLANK	1
39	23	S	BLANK	1
40	24	QC1	STD-0.10	1
41	25	QC2	STD-1.0	1
42	0	N	Null	1
43	7	S	0.05	1
44	9	S	ERA 0.1	1
45	10	S	ERA Nutrient	1
46	11	S	ERA 2.0	1
47	0	N	Null	1
48	0	N	Null	1
49	8	S	STD-0.00	1
50	7	S	STD-0.05	1
51	6	S	STD-0.1	1
52	5	S	STD-0.3	1
53	4	S	STD-0.5	1
54	3	S	STD-1.0	1
55	2	S	STD-2.0	1
56	1	S	STD-3.0	1
57	0	N	Null	1
58	2	D	Drift	1
59	0	E	End	1

Page 2

Figure 4-6. Example of a tray protocol.

16. Select “Run” from the pulldown menu, or the “Run” button on the system window.

17. Select “Start” from the menu.

18. Select the .run file for the run to be analyzed.

19. Click the “OK” button to start the run.

20. Monitor the run and check the correlation coefficient of the standard curve as soon as the standards have been run. It will appear in the lower left corner of the charting window. If it is < 0.995, retrieve the curve by clicking the cablibration curve button on the charting window (Figure 4-7. If a standard falls off of the line, stop the run, correct the problem and restart the run. Click “OK” to close any warning dialog windows that appear to alert you to the fact that a control is out of range. The control will usually pass when the final corrections are made.

21. Click “OK” in the dialog box when the run is finished. The data and text files will be generated and saved. The report and calibration curve will print automatically.

22. After all analysis runs are complete, the reagent tubes can be moved to the rinse bottle filled with DDW. Cap all the reagent bottles and store in the refrigerator. Let the system rinse for one hour. Then, select the pump icon in the system 1 window and click “Off” to turn off the pump. Charting must be active to access the system icons. The instrument and computer are generally left on during routine analysis. Turn off power to the monitor when finished for the day to prevent possible screen damage.

For prolonged shut-down (more than 2 days), turn off the computer, the TRAACS analyzer and the autosampler.

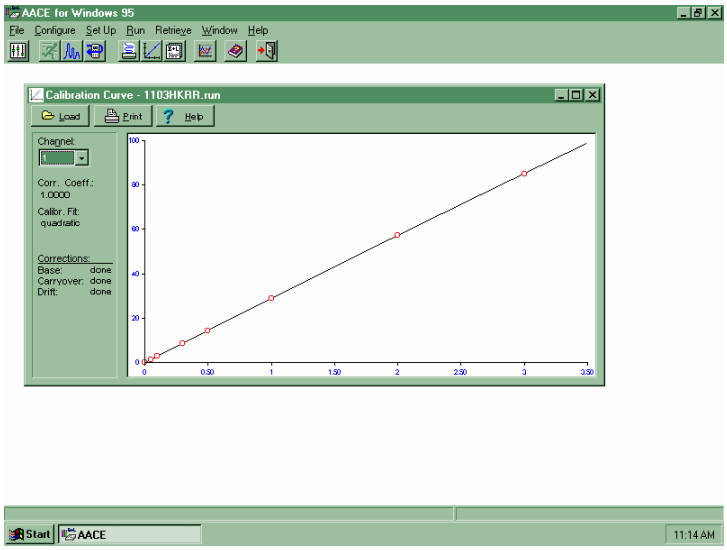


Figure 4-7. Example of retrieved calibration curve.

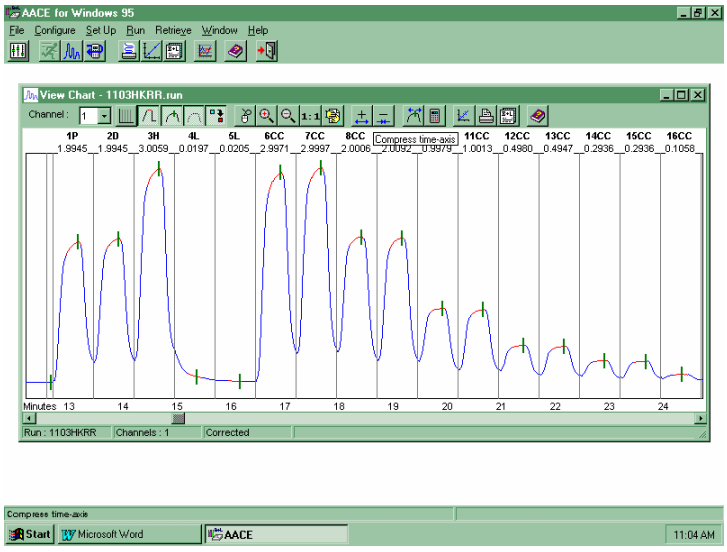


Figure 4-8. Example of retrieved chart.

5.0 QUANTIFICATION

5.1 Data Calculation

1. Minimize or exit Aace.

2. Double click the Fox Pro “NH4 Calc” icon on the desktop.

3. Enter the file name of the run to be calculated.

4. Enter the extraction volume (10 or 15).

5. Maximize the Fox Pro file window.

6. Enter any flags, delete samples, modify extraction volumes or area factors and recalculate, or perform any other changes necessary to complete the data file.

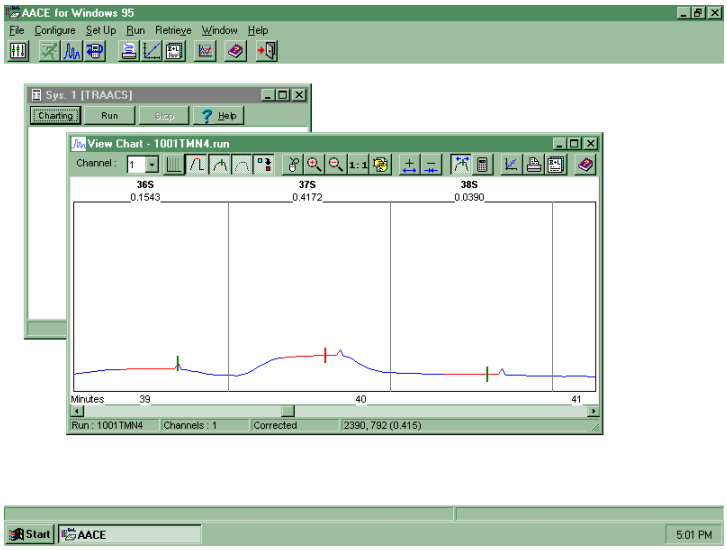


Figure 5-1. Corrected peaks.

7. Close the data file.

8. Archive the file on a 3 1/2' floppy.

9. Transfer the file to the network, calculate precision, and update the status sheet.

5.2 Reanalysis of Data

It may be necessary to correct the position of a peak maker due to it being incorrectly positioned. Bubbles hanging in the cell, particles, or disturbances in the bubble pattern may result in the peak being picked at an inappropriate place on an otherwise useable peak. Correction is accomplished by retrieving the chart, repositioning the peak marker(s), recalculating and saving the run, exporting the data to a text file, and running NH4 Calc on the text file. Details on this procedure may be found in Sections 8.2 and 4.2 of the Aace Operation Manual or by accessing the Help files within the Aace software.

6.0 QUALITY CONTROL

The quality control procedures serves two purposes: 1) to identify possible problems with the measurement process, and 2) to calculate the precision of ion measurements.

6.1 Tolerances and Actions to be Taken

Tolerances are generally ±30% at levels between 0.030 and 0.100 mg/ml; ±20% at levels between 0.100 and 0.150 mg/ml; and ±10% at levels above 0.150 mg/ml. If replicates exceed these tolerances, analyses beyond the last acceptable replicate are suspected to be incorrect. The replicate analysis on the same sample should be repeated again. If the second replicate duplicates, the original sample result, the first replicate result can be taken as spurious. If the second replicate matches the first replicate then another replicate should be selected from that set of 10 samples to check if the original value was a spurious result, and should be analyzed to verify that assumption. If the second replicate analysis exceeds the tolerance criteria, the cause of the error (probably in the instrument or the chemistry of the analysis) must be determined. Then, the whole set of samples after the last acceptable replicate must be reanalyzed. Notify the laboratory supervisor immediately if sample rerun is to be performed.

6.2 Data Validation Feedback

The sample validation philosophy follows the three-level approach devised by Mueller and Hidy et al., (1983) in the Sulfate Regional Experiment (SURE). Level I sample validation takes place in the field or laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred, 2) verifying computer file entries against data sheets, 3) eliminating values from measurements which are known to be invalid because of instrument malfunctions, 4)

replacing data when re-analyses have been performed, and 5) adjusting measurement values for quantifiable calibration of interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master data base. Level II applies consistency tests based on known physical relationships between these variables in the assembled data.

Level III sample validation is part of the data interpretation process and will be performed by each project manager and subsequent data users. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause.

The laboratory supervisor should review all the QC data as soon as it becomes available and ensure the feedback from the QC results to the routine operations. The project manager should consult with the QA officer to initiate and document changes to the data base as they are needed.

7.0 QUALITY ASSURANCE

The performance and system audits are scheduled on a biannual basis by the QA officer to ensure that all procedures are followed properly and to verify the precision, accuracy and validity of the data.

8.0 REFERENCES

Berthelot (1855). Berthelot, M.P. Rep. Chim. Appl. 1855, p. 284

ACS (1983). American Chemical Society Committee on Environmental Quality , Principles of Environmental Analysis. Analytical Chemistry 55: 2210-2218.

Bran + Luebbe (1988). Bran+Luebbe Analyzing Technologies, Technicon Industrial Systems, "TRAACS 800 Continuous-Flow Analytical System: Operation Manual," Technical Publication DSM-0005-00.5, Version 3.03, August, 1988.

Bran+Leubbe (1997) Aace Software Operation Manual. Publication No. MT7-18EN-03. December 1997. Bran+Leubbe GmbH Werkstrasse 4, 22844 Norderstedt, Germany.

Watson, J.G., J.C. Chow, L.W. Richards, S.R. Anderson, J. E. Houck, and D.L. Dietrich (1988). "The 1987-88 Metro Denver Brown Cloud Air Pollution Study, Volume II: Measurement." DRI Document No. 8810.1F2, prepared for the Greater Denver Chamber of Commerce, Denver, CO, by Desert Research Institute, Reno, NV.

APPENDIX A.9

DRI STANDARD OPERATING PROCEDURE

Pages: 397
Date: 4th Qtr. 1994

Title: Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy

Number: 2-206.3
Revision: 3

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are: 1) to provide a basic understanding of the principles of operating the atomic absorption spectrophotometer (AAS); 2) to describe routine analysis for trace metals (i.e., Na^{+}, Mg^{++}, K^{+}, Ca^{++}) in aqueous filter extracts or precipitation samples using the Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer; and 3) to codify the actions which are taken to implement a state-of-the-art atomic absorption spectrophotometric measurement process. This procedure is to be followed by all analysts in the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute.

1.2 Measurement Principle

Atomic absorption spectrophotometry resembles emission flame photometry in that a sample is aspirated into a flame and atomized. In flame photometry, the amount of light emitted is measured, whereas in atomic absorption spectrophotometry, the amount of light absorbed is measured. A light beam from a hollow cathode lamp is directed through the flame, into a monochromator, and onto a photoelectric detector that measures the amount of light absorbed by the atomized element in the flame. The cathode of a hollow cathode lamp contains the pure metal which results in a line source emission spectrum. Since each element has its own characteristic absorption wavelength, the source lamp composed of that element is used. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample. Both atomic absorption and atomic emission can be measured using Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer.

1.3 Measurement Interferences and Their Minimization

1.3.1 Chemical Interferences

Major interferences can be caused by competition between molecular association and dissociation in the flame. This occurs when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. A high temperature flame provides additional energy to break down the compounds. Alternatively, this type of chemical interference

can be controlled by the addition of a releasing agent to the sample and standard solutions. The releasing agent (or competing cation) added to the sample solution will preferentially react with the interferant and remove the interference.

Lanthanum can be added to the aqueous sample or sample extract before aspiration to eliminate the interference of phosphate and silicates in the calcium (Ca^{++}) determination. Because nitric acid enhances the signal for the determination of calcium, this acid must also be added to both the sample extracts and calibration standards. Lanthanum is also used to eliminate the interference of phosphorus, silicon, titanium and aluminum sulfate in the determination of magnesium (Mg^{++}).

1.3.2 Ionization Interferences

Ionization interferences occur when the flame temperature has enough energy to remove an electron from the atom, creating an ion. This depletes the number of ground state atoms which are absorbing the incident light, thus reducing the absorption of the incident light by the atoms. The overall effect is to reduce the sensitivity of the method. The addition of easily ionized elements, in much higher concentrations than the ion to be analyzed, to both calibration standard solutions and sample extracts can eliminate the ionization interferences. The addition of cesium chloride to the aqueous sample or sample extract before aspiration is necessary to overcome ionization interferences in the determination of sodium (Na^{+}) and potassium (K^{+}).

1.3.3 Matrix Interferences

Matrix interferences occur when the physical characteristics (i.e., viscosity, surface tension, burning characteristics) between the sample solutions and calibration standard solutions differ substantially. This is common when there are high concentrations of dissolved salts or acids in the sample solutions.

Diluting the sample, matching the matrix components in both sample and calibration standard solutions (i.e., adding the same reagent to both sample and calibration standard solutions), or adding methanol to the solutions are procedures which may eliminate matrix interferences.

1.3.4 Dissimilar Standards

Calibration standard solutions must be matched as nearly as possible to the sample solutions in important matrix components such as additives and pH.

1.4 Ranges and Typical Values of Measurement Obtained by this Procedure

A wide range of ambient concentrations can be found in both the filter extracts and precipitation samples. Table 1-1 summarizes the ranges and typical values of measurement obtained from the past studies.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The minimum detection limits of Na^+, K^+, Mg^{++}, and Ca^{++} are 0.005, 0.010, 0.003, and 0.025 □g/ml, respectively. The Lower Quantifiable Limits (LQLs) for each species listed in Table 1-1 is equal to the standard deviation of field blank filter concentrations or the minimum detection limit (ACS, 1983), whichever is greater.

Accuracy and precision of AAS depend on the sample and standard matrix, element of interest, and other instrument parameters such as the wavelength selected, the purity of the gases as well as the flame type and conditions. In general, the accuracy of AAS is primarily limited by the uncertainties in the standard solution preparation, typically within ±10%. Precisions depend on the species analyzed because sensitivity varies with analyte. Sodium and potassium have approximately the same sensitivity, so the expected precisions for these two elements are the same: ±30% for concentrations less than 0.100 □g/ml; ±20% for concentrations between 0.100 and 0.150 □g/ml; and ±10% for concentrations greater than 0.150 □g/ml. Calcium is approximately ten times less sensitive under the instrument conditions currently used,

Table 1-1

Typical Ranges and Values of Atomic Absorption Measurements with Minimum Detectable and Quantifiable Limits

	Concentrations in mg/m^3			
Chemical Species	Range of Urban Concentrations	Range of Non-Urban Concentrations	Minimum Detectable Limit[a]	Lower Quantifiable Limit[b]
Soluble Na^+	0.2 to 5[c]	0.07 to 0.3[c]	0.05[d]	0.005[d]
Soluble Mg^{++}	0.07 to 0.7[c]	0.03 to 0.1[c]	0.0008[d]	0.010[d]
Soluble K^+	0.07 to 0.7[c]	0.07 to 0.5[c]	0.07[d]	0.003[d]

Soluble Ca^{++}	0.11 to 1.3[c]	0.1 to 0.4[c]	0.05[d]	0.025[d]

[a] Minimum Detectable Limit (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero.

[b] Lower Quantifiable Limit (LDL) equals three times the standard deviation of dynamic field blanks as determined from previous monitoring programs.

[c] Preliminary data from CADMP sites for PM_{10} samples.

[d] Assumes extraction of half filter in 15 ml and 15 m^3 air volume.

so the precision ranges would be expected to shift by that factor: ±30% for concentrations less than 1.000 □g/ml; ±20% for concentrations between 1.000 and 1.500 □g/ml; and ±10% for concentrations greater than 1.500 □g/ml. Magnesium is roughly twice as sensitive, so the precision ranges would shift correspondingly: ±30% for concentrations less than 0.050 □g/ml; ±20% for concentrations between 0.050 and 0.100 □g/ml; and ±10% for concentrations greater than 0.100 □g/ml.

1.6 Responsibilities of Personnel for Carrying Out Portions of This Procedure

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing AA analysis. The analyst must follow the procedure for routine system calibrations, chemical analysis, and performance tests.

It is the responsibility of the laboratory manager to ensure that the AA analysis procedures are properly followed, to examine all replicate, standard, and blank performance test data, to designate samples for re-analysis, and to deliver the analysis results to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible for determining the extent and methods of quality assurance to be applied to each project, for estimating the level of effort involved in this quality assurance, for identifying the appropriate personnel to perform these QA tasks, for updating this procedure periodically, and for ascertaining that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used in this document:

Atomic Emission:	The flame converts the sample aerosol into an atomic vapor and then thermally elevates the atoms to an excited state. When these atoms return to the ground state, they emit light which is detected by the instrument. The intensity of light emitted is proportional to the concentration of the element of interest in the sample.
Atomic Absorption:	The flame converts the sample aerosol into an atomic vapor which can absorb light from the primary light source. The amount of light absorbed is proportional to the concentration of the element in the sample.
Hollow Cathode Lamp:	The primary light source which emits high intensity narrow-line spectra of the element of interest. The cathode of a hollow cathode lamp is constructed with a pure metal of the selected element. Two elements can be used in one lamp to reduce time spent changing

lamps. DRI laboratory uses a K/Na lamp and a Ca/Mg lamp.

Double-Beam System: The light from the source lamp is divided into a sample beam, which is focused through the sample cell, and a reference beam, which is directed around the sample cell. The read out represents the ratio of the sample and reference beams. Thus, fluctuations in source intensity do not become fluctuations in instrument readout and a more stable baseline can be achieved.

Nebulizer: A system in which the sample is aspirated into the instrument and broken into tiny droplets for delivery into the flame.

Burner chamber: The area in which the flame gases are mixed with the sample and swept up into the burner head.

Burner head: The section of the burner at which the flame is generated. One burner head is required for use with the air/acetylene flame (10 cm, PE # 0040-0266) and another for use with the nitrous oxide/acetylene flame (5 cm, PE #0040-0277).

Autosampler: A microprocessor controlled carousel and probe which automatically delivers up to 50 samples to the nebulizer.

Optimum Concentration Range: Defined by limits expressed as concentrations, below which background noise swamps the analyte signal and above which curve correction should be used. This range varies with the sensitivity of the method for the analyte.

Sensitivity: The sensitivity is defined as the concentration of the metal analyte in □g/ml which produces an absorbance of 1% (approximately 0.0044 absorbance units). For the Perkin-Elmer 2380, the sensitivity for sodium is 0.006 □g/ml; for potassium, it is 0.01 □g/ml; for magnesium, 0.003 □g/ml; for calcium, 0.05 □g/ml.

Detection Limit: The concentration of an element which would yield an absorbance equal to three times the standard deviation of the response to a known concentration of zero (ACS, 1983).

1.8 Related Procedures

Related laboratory procedures are specified in the following DRI Standard Operating Procedures. Materials Sefety Data Sheets for chemicals used in this procedure should also be consulted.

DRI SOP # 2-201.2 Sectioning of Filter Samples
DRI SOP # 2-202.2 Extraction of Ionic Species from Filter Samples

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The Perkin Elmer (PE) Atomic 2380 Absorption Spectrophotometer (AAS) double beam instrument consists of 5 main parts as shown in Figure 2-1.

- Light Source: Emits the line-spectrum of the element of interest.
- Absorption Cell: Cell in which atoms of the sample are produced via a flame.
- Monochromator: A grating used for isolating an emission line from the lamp to be used for absorption.
- Photoelectric Detector: Measures the light intensity and amplifies the signal.
- Display: Shows the reading after it has been processed by the instrument electronics.

Additional required equipment include the exhaust vent, autosampler, computer, and printer.

- A venting system is required to remove the fumes and vapors from the flame or furnace of atomic absorption instruments. A flow rate of 5400-5800 lpm is used for the AAS venting system. The exhaust vent is used to: 1) protect laboratory personnel from toxic vapors produced by some samples; 2) protect the instrument from corrosive vapors from aspiration of the sample; 3) improve flame stability by removing laboratory drafts; and 4) remove heat generated from the flame.
- The Perkin Elmer Model AS-50 Flame Auto Sampler is used for analysis using the flame. This consists of a transport mechanism (sample carousel)

and a control unit. The sample carousel holds up to fifty 15 ml sample tubes, three standards and a wash beaker. Sampling is performed by a probe which is connected to the nebulizer.

- An IBM compatible personal computer (PC) is used to automatically record the absorbance data of the calibration standards and samples in order as they are analyzed.

- A printer connected to the PC generates a hard copy of the absorbance data as the samples are analyzed.

2.1.2 Instrument Characterization

The PE 2380 AAS and AS-50 autosampler analyzes the contents of as many as 50 sample tubes per run, including an auto zero and up to 3 calibration standards if the instrument is used in the CONCENTRATION mode. In the ABSORBANCE mode, as many standards as desired are used to establish the calibration curve. Currently, one blank and 7 standards are used.

Figure 2-1. Perkin Elmer model 2380 AA optical schematic.

The autosampler controller is used to set a read delay time to allow time for the sample to travel through the sample tube into the flame and for the subsequent signal to stabilize. The read time is also set at a level long enough to permit the required number of readings to be taken.

The PE 2380 AAS instrument controls are used to select the proper lamp current, gain and wavelength. The flame gases are controlled from the Interlocked Gas Control System. The signal resulting from the samples can be received in Absorbance, or Concentration. Absorbance is used since this permits the original signal to be captured on the computer.

The integration time, numbers of readings to be taken per sample, and reporting of average and standard deviation can be selected on the PE 2380 AAS.

The location of the burner head and flow rate through the nebulizer must be optimized. Since the samples analyzed are all aqueous solution, these adjustments are performed only after the burner system is cleaned.

2.1.3 Maintenance

Regular maintenance of the PE 2380 includes the following:

- The burner chamber must be rinsed with water after each set of analyses by aspirating water through the system with the flame lit for 5 minutes after analysis is complete.

- At the end of each full week of analyses, the burner chamber and burner head must be rinsed more thoroughly by removing the burner head, sonicating it for one hour and gently scraping any salt deposits off the burner surface. While the head is off, the chamber itself is cleaned by pouring 250 ml DDW through the top of the chamber.

- Occasionally, a sputtering sound can be heard when the flame is first lit after thorough cleaning. This indicates either incorrect seating of the burner head or water in the system. Water may be at the nebulizer outlet after washing. Allow the air to vent through the burner chamber for 15 minutes without the flame being lit to aid in drying. If the system is expected to be dry after sitting for an extended period, check for incorrect seating by removing the burner head and reseating it. If the sputtering sound persists, the O-ring at the top of the chamber which seals the burner head seat may need to be replaced (PE #303-6095).

- The drain bottle under the instrument must be checked at the beginning of each analysis day. If the level of waste is at the shoulder of the bottle, the bottle must be emptied to the 8 liter mark on the side. Because the samples are all aqueous, without significant adjustment of pH or other characteristics, the waste may be poured directly down the sink.

- The high performance Platinum\Iridium nebulizer, (PE#B050-5480) is cleaned according to the Perkin Elmer high performance nebulizer handbook instructions. (Publication#B3112).

- If the signal seems noisy, the burner head is cleaned as above, the chamber location is readjusted. If the signal suddenly drops, a clog in the nebulizer or sample delivery tube is suspected. The nebulizer can be cleaned with the brass cleaning wire provided with the nebulizer.

- Printer paper should be checked before the beginning of each analysis run to ensure that a sufficient quantity is in place for the run.

- The printer ribbon should be checked and changed when the print quality changes from dark black to light black.

- Work areas should be kept clean.

- Additional maintenance and trouble shooting information can be found in the Perkin Elmer 2380 Instruction Manual (Perkin Elmer, 1977).

2.1.4 Laboratory Supplies and Spare Parts

- Compressed air supply: Minimum of 28 lpm flow rate at a minimum pressure of 40 PSI. DRI's building compressed air supply is used after it

has passed through an oil trap, a particulate filter, and a regulator set at 75 psi. The compressed air is used as the oxidant for the air/acetylene flame.

- Acetylene: Obtained in size 1B cylinders containing about 9000 liters (STP) of gas dissolved in acetone. The acetylene flow is 4 lpm with a heat combustion value of 1450 BTU per cubic foot. Suitable acetylene has a minimum purity of 99.6 to 99.8%. Air/acetylene is the preferred flame for the determination of approximately 35 elements by atomic absorption. Replace the acetylene tank when the pressure is at 520 PSI. This residual pressure is due to the acetone solvent.

- Nitrous Oxide: Obtained in size 1A cylinders containing about 15,000 liters (STP). The nitrous oxide is in a liquid state with an initial pressure at 750 psi. The gas above the liquid is drawn off for use in the instrument. After all the liquid has evaporated, the pressure falls rapidly as the remaining gas in the cylinder is drawn off. Nitrous oxide/acetylene flame requires a flow rate of 20 lpm nitrous oxide. The size 1A cylinder of nitrous oxide lasts for about 12 hours of operation.

- Volumetric flasks: Class B polymethylpentene volumetric flasks, 100 ml (±0.16 ml accuracy).

- Pipettes: Class A volumetric in 1, 2, 3, 5 and 10 ml sizes.

- Micropipettes: Eppendorf pipets in 1000 □l, 500 □l, 200 □l and 100 □l with disposable pipet tips.

- Volumetric micro syringe: Hamilton 50 □l (Hamilton, Reno, NV 89510 #705, 50□l).

- Wide mouth bottles: Polyethylene, 125 ml. Used for storage of calibration and working standards.

- Polyethylene centrifuge tubes: 15 ml, used in the autosampler.

- Disposable beakers: Polystyrene, 10 ml.

- Spare lamps: Na-K, PE# 303-6095; Ca-Mg, PE# 303-6092 (Perkin Elmer, Norwalk, CT).

- Spare burner head O-rings: PE# 990-2219 (Perkin Elmer, Norwalk, CT).

- Spare probes: Stainless Steel PE# 047-1422 (Perkin Elmer, Norwalk, CT).

- Spare sample tubing: Polyethylene PE# B015-6272 (Perkin Elmer, Norwalk, CT).

- Spare impact bead: Corundum (Al_2O_3) PE# B050-5086 (Perkin Elmer, Norwalk, CT).

- Spare flow spoiler: Polyethylene, PE#0057-2561 (Perkin Elmer, Norwalk, CT).

- Printer ribbons.

- Printer paper.

2.2 Reagents

2.2.1 Use analytical grade chemicals for all solutions.

Distilled-deionized water (DDW) conforming to ASTM specification D1193, Type II (Annual Book of ASTM Standard, 1983).

Nitric Acid (HNO_3): Concentrated, ACS reagent grade.

Cesium Chloride (CsCl): ACS reagent grade, 99.9% pure.

Lanthanum Nitrate Hexahydrate ($La(NO_3)_3 \cdot 6H_2O$): ACS Reagent grade 99.9% pure.

Stock calibration standard solutions: Certified, Fisher Scientific, Fair Lawn, NJ 07410 or Perkin Elmer , Norwalk, CT.

Na, 1000 □g/ml
K, 1000 □g/ml
Ca, 1000 □g/ml
Mg, 1000 □g/ml

Ethanol: Reagent grade, anhydrous (of the type suitable for histological use).

2.2.2 Preparation of Solutions

When solutions are prepared, label the container with the contents, concentration, date prepared, and preparer's initials.

In transferring solutions for dilutions, pour the concentrated solution into a disposable beaker. Rinse the volumetric pipet to be used with this solution in the beaker. Pour a new aliquot of solution into a different disposable beaker and pipet from this beaker using the volumetric pipet rinsed with the solution

into the volumetric flask. This procedure minimizes contamination due to inserting pipets or other objects into the solution.

Use glassware and plasticware which has been properly washed using a dilute Alconox solution (0.1 g in approximately 4 liters distilled water) and rinsed with DDW until the detergent is no longer visible, then rinsed with DDW at least three more times.

2.2.2.1 Cesium Chloride Stock Solution (1% w/v Cs):

Before preparing the Cs Stock Solution from a new batch of reagent, test the new batch of reagent for the presence of the elements to be analyzed by preparing at least two 10 ml test samples at different concentrations as follows:

%Cs	Weight CsCl/10 ml DDW
Blank	0
0.1%	0.01268 g
2.5%	0.3167 g
5.0%	0.6333 g

Test these solutions for the presence of the element of interest using the AAS. An absorbance of less than 0.010 absorbance units at the 0.1% level is acceptable since the standards and samples will be matched in Cs concentration.

To prepare the Cesium Stock Solution (1% w/v), weigh 6.335 g CsCl (to the nearest 0.001 g) into a disposable weighing boat. Transfer the chemical quantitatively into a 500.00 ml flask by rinsing it into the flask with DDW from a wash bottle. Fill to the 500.00 ml mark with DDW. This solution is used to produce standards and samples of 0.1% Cs concentration. The Cs acts as an ionization suppressant in the K^+ and Na^{++} analyses.

2.2.2.2 Lanthanum Nitrate Hexahydrate ($La(NO_3)_3.6H_2O$) (1% w/v La) Stock Solution:

Before preparing the La Stock Solution, test the new batch of reagent for the presence of the elements to be analyzed by preparing at least two 10 ml test samples at different concentrations as follows:

%La	Weight $La(NO_3)_3 \cdot 6H_2O$/10 ml DDW
Blank	0
0.1%	0.03116 g
2.5%	0.7791 g
5.0%	1.5581 g

Test for the presence of any elements of interest by measuring the absorbance on the AAS. An absorbance of less than 0.010 units at the 0.1% level is acceptable since the standards and samples will be matched in La concentration.

To prepare the Lanthanum Stock Solution (1% w/v), weigh 15.600 g lanthanum nitrate hexahydrate (to the nearest 0.001 g) into a disposable weighing boat. Transfer the chemical quantitatively to a 500 ml volumetric flask by rinsing it into the flask with DDW from a wash bottle. Fill to the 500.00 ml mark with DDW.

This solution is used to produce standards and samples of 0.1% La concentration. The La acts as an interference suppressant for phosphate, aluminum and silicate in the Mg^{++} and Ca^{++} analyses.

2.2.2.3 Combined Lanthanum/Cesium stock solution (1% w/v La and 1% w/v Cs):

To prepare the Lanthanum/Cesium combined Stock Solution (1% w/v La and 1% w/v Cs), weigh 15.600g lanthanum nitrate hexahydrate (to the nearest 0.001g) into a disposable weighing boat. Quantitatively transfer the solid into a 500.00 ml volumetric flask using DDW. Then, weigh 6.335 g CsCl (to the nearest 0.001 g) into a disposable weighing boat. Transfer the chemical quantitatively to a 500 ml volumetric flask by rinsing it into the flask with DDW from a wash bottle. Dissolve the combined solids in about 250 ml DDW. Fill to the 500.00 ml mark with DDW and mix thoroughly by inverting the flask at least 10 times and swirling each time. Transfer the solution into a 500 ml high density polypropylene bottle by rinsing the clean bottle three times with small portions of the solution and discarding the rinses, then pouring the solution into the storage bottle. Store in the refrigerator. This solution is stable indefinitely, so prepare as needed when the solution is depleted. Before using, check for any contamination by preparing the AA BLANK as described below in Section 3.1.6.

This solution is used to produce standards and samples of 0.1% La and Cs concentration. The La acts as an interference suppressant from phosphate, aluminum and silicate in the Mg^{++} and Ca^{++} analyses, and the Cs acts as an ionization suppressant in the analysis of Na^{+} and K^{+}.

2.2.2.4 Nitric acid (HNO_3), 1.6M:

Dilute concentrated nitric acid (16M) by pipetting 10.00 ml into a 100.00 ml volumetric flask. Dilute to the mark with DDW. This solution is used to prepare standards and samples with concentrations of 0.016 N HNO_3 for the analysis of Ca.

2.3 Forms and Paperwork

A sample analysis list will be prepared by the laboratory manager indicating which samples will be analyzed and any special instructions (Figure 2-2). Samples designated for atomic absorption spectrophotometry (AA) analysis are logged into the "AA Analysis Logbook," as are notes concerning the preparation of standards and maintenance (Figure 2-3).

The samples are listed in a run list (Figure 2-4) (see also section 4.3.1). The samples are loaded into the autosampler from this list. The sample ID's are correlated with the absorbencies generated in the

Figure 2-2. DRI sample analysis list.

Figure 2-3. DRI AA analysis logbook format.

Figure 2-4. DRI AA run list.

computer print out of the absorbencies by recording the number of the analysis (Computer Run #) on the run list next to the Sample ID in the column indicated. Using this run list, the sample ID's are finally combined with the computer run numbers in the data base of the absorbance and concentrations produced in the calculations (Section 5).

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

Stock Standard Solutions are either purchased as certified solutions or prepared from ACS reagent grade materials. These solutions are properly labeled with the name of the chemicals in the solution, the concentrations, the initials of the person making them, and the date solution was made. Solutions are then stored in the refrigerator in high density polyethylene or polypropylene containers. Discard the solutions after a year. All standard solutions (stock, working standards (WS), and calibration standards) should be removed from the refrigerator and allowed to come to room temperature before using or diluting.

In transferring solutions for dilutions, pour the concentrated solution into a disposable beaker. Rinse the volumetric pipet to be used with this solution in the beaker. Pour a new aliquot of solution into a different disposable beaker and, using the rinsed volumetric pipette, pipet from this new beaker into the volumetric flask.

Use glassware and plasticware which has been properly washed using a dilute Alconox solution (0.1 g in approximately 4 liters distilled water) and rinsed with DDW until the detergent is no longer visible, then rinsed with DDW at least three more times.

3.1.1 Stock Solutions

Stock Standard Solutions for Na^+, Mg^{++}, K^+, and Ca^{++} are purchased as certified, ACS reagent grade material from Fisher in 1000 □g/ml concentrations.

3.1.2 Working Standards (50 and 5 □g/ml WS)

These are intermediate standard solutions used for making calibration stds for the AAS calibration curve. Working standards are prepared from the stock solutions for use within one month and stored in the refrigerator. Make up four working standard solutions: one 50.00 □g/ml in Na^+ and K^+, one 50.00

□g/ml in Ca^{++} and Mg^{++}, one 5.00 □g/ml in Na^{+} and K^{+}, and one 5.00 □g/ml in Ca^{++} and Mg^{++},

- Preparation of 50.00 □g/ml Na/K Working Standard (50 Na/K WS). Pipet 5.00 ml (using a 5.00 ml volumetric pipet which has been rinsed with the solution to be pipetted as described in section 3.1) of each of the 1000 µg/ml stock solutions of Na^{+} and K^{+} from disposable beakers filled with the solutions into a 100.00 ml polypropylene volumetric flask and fill to volume with DDW. Mix well by inverting the flask 10 times and swirling each time. The final concentration of the solution is 50.00 □g/ml each of Na^{+} and K^{+}. Store in refrigerator.

- Preparation of 50.00 □g/ml Ca/Mg Working Standard (50 Ca/Mg WS). Pipet 5.00 ml (using a 5.00 ml volumetric pipet which has been rinsed with the solution to be pipetted as described in section 3.1) of each of the 1000 µg/ml stock solutions of Ca^{++} and Mg^{++} from disposable beakers filled with the solutions into a 100.00 ml polypropylene volumetric flask and fill to volume with DDW. Mix well by inverting the flask 10 times and swirling each time. The final concentration of the solution is 50.00 □g/ml each of Ca^{++} and Mg^{++}. Store in refrigerator.

- Preparation of 5.00 □g/ml Na/K Working Standard (5 Na/K WS). A second working standard is needed for dilute standards. Make a 5.00 □g/ml WS by pipetting from a disposable beaker filled with the 50 Na/K WS (with a 10.00 ml volumetric pipet which has been rinsed with the solution to be pipetted as described in section 3.1) 10.00 ml of the 50.00 □g/ml Na/K WS into a 100.00 ml polypropylene volumetric and fill to volume with DDW. Mix thoroughly by inverting the stoppered flask 10 times and swirling each time. Store in refrigerator.

- Preparation of 5.00 □g/ml Ca/Mg Working Standard (5 Ca/Mg WS). A second working standard is needed for dilute standards. Make a 5.00 □g/ml WS by pipetting 10.00 ml (with a 10.00 ml volumetric pipet prepared by rinsing with the solution to be pipetted as described in section 3.1) of the 50.00 □g/ml Ca/Mg WS from a disposable beaker filled with the solution into a 100.00 ml polypropylene volumetric and fill to volume with DDW. Mix thoroughly by inverting the stoppered flask 10 times and swirling. Store in refrigerator.

3.1.3 Calibration Standards for atomic absorption analysis for sodium and potassium ONLY:

Prepare calibration standards in sodium and potassium concentrations of 0, 0.025, 0.050, 0.100, 0.250, 0.500, 1.000, and 1.500 µg/ml. Use 100.00 ml polymethylpentene or polypropylene volumetric flasks. Store calibration standards in the refrigerator. Prepare as needed as the solutions are depleted.

In preparing to pipet, proceed with rinsing the volumetric pipets with the appropriate WS from a disposable beaker. Pipet from another disposable beaker filled with a second portion of the solution to be pipetted.

After the volumetric flasks are filled to volume with DDW, stopper the flasks and mix each one thoroughly by inverting each one 10 times and swirling each time.

- Blank Solution: Add 10.00 ml 1% w/v Cs Stock Solution (using a 10.00 ml volumetric pipet) to 100.00 ml volumetric flask and bring to volume with DDW.

- 0.025 □g/ml: Add 10.00 ml 1% w/v Cs Stock Solution to 100.00 ml volumetric flask; then using a 0.500 ml Eppendorf pipet (use the balance to confirm the volume by weight), pipette 0.500 ml 5 □g/ml Na/K WS into the flask and bring to volume with DDW. If volume and weight are not the same,either record weight of standard and calculate actual concentration, or weigh 0.500g ± 1%. Do weight/volume comparisons for all calibration stds.

- 0.050 □g/ml: Add 10.00 ml 1% w/v Cs Stock Solution to 100.00 ml volumetric flask, then pipette 1.00 ml (1.00 g) of 5 □g/ml Na/K WS into the flask and bring to volume with DDW.

- 0.100 □g/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml volumetric flask, then pipette 2.00 ml (2.00 g) of 5 □g/ml Na/K WS into the flask and bring to volume with DDW.

- 0.250 □g/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml volumetric flask, then pipette 5.00 ml (5.00 g) of 5 □g/ml Na/K WS into the flask and bring to volume with DDW.

- 0.500 □g/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml volumetric flask, then pipette 10.00 ml (10.00 g) of 5 □g/ml Na/K WS (or 1.00 ml (1.00 g) of 50 µg/ml) into the flask and bring to volume with DDW.

- 1.000 □g/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml volumetric flask, then pipette 2.00 ml (2.00 g) of 50 □g/ml Na/K WS into the flask and bring to volume with DDW.

- 1.500 □g/ml: Add 10 ml 1% Cs Stock Solution to 100.00 ml volumetric flask, then pipette 3.00 ml (3.00 g) of 50 □g/ml Na/K WS into the flask and bring to volume with DDW.

3.1.4 Preparation of calibration standards for analysis for calcium and magnesium ONLY:

Prepare calibration standards in concentrations of calcium and magnesium of 0, 0.025, 0.050, 0.100, 0.250, 0.500, 1.000, and 1.500 □g/ml. Use 100.00 ml polymethylpentene or polypropylene volumetric flasks. Store calibration standards in the refrigerator. Prepare as needed as the solutions are depleted.

Prepare as for Sodium/Potassium standards, but add 10 ml 1% La Stock Solution to 100.00 ml polyethylene volumetric flasks, add 1 ml 1.6N HNO_3, then pipette in the appropriate amounts of the Calcium/Magnesium 5 □g/ml and 50 □g/ml WS as above. Check to see that weight and volume match.

3.1.5 Preparation of calibration standards for analysis for calcium, magnesium, sodium and potassium

For analysis of teflon (or teflon type) filters, the filters are first wetted with 200 □l ethanol (EtOH) and extracted in a 10 ml matrix solution of 0.1% La, 0.1% Cs and 0.016 N HNO_3 in DDW. The standards must match the samples in matrix, including the addition of 200 □l EtOH per 10 ml of calibration std. solution. Because ethanol has a high vaporization rate, it is added to the calibration standards only when teflon filters are being analyzed. Dilution factor for these calibration standards with added EtOH (20 µl/ml of standard) is consequently adjusted (DF = 1.00 ml std. + 0.10 ml La/Cs + 0.02 ml EtOH = 1.12).

If a filter type other than Teflon is used, prepare the standards so they duplicate the samples in all matrix components. For analysis, the samples and standards must contain the matrix modifiers (Cs ionization suppressant, La releasing agent, nitric acid for the Ca analysis). Matching the samples and standards may require preparation of standards as required for the analysis and modifying the matrices of the samples to match.

Prepare calibration standards with concentrations of calcium, magnesium, sodium and potassium of 0, 0.025, 0.050, 0.100, 0.250, 0.500, 1.000, and 1.500 □g/ml. Use 100.00 ml polymethylpentene or polypropylene volumetric flasks. Store calibration standards in the refrigerator. Prepare as needed as the solutions are depleted. Calibration standards prepared in acidic solutions, stored in high density polypropylene bottles are stable for at least 3 months if kept uncontaminated. Calibration standards containing ethanol tend to be unstable , with a very short shelf life. If these older calibration standards are to be used, prepare at least two new calibration standards just prior to analysis to check that the calibration standards have not become contaminated.

Prepare as for Sodium/Potassium standards, but add 10 ml 1% La/Cs Stock Solution, and 1.00 ml 1.6N HNO_3, to each 100.00 ml polypropylene volumetric flask. Then pipette in the appropriate amounts of the

calcium/magnesium 5 □g/ml and 50 □g/ml WS and the appropriate amounts of the sodium/potassium 5 □g/ml and 50 □g/ml WS as above. Weights and volumes must match as they do for all other standards. Before diluting to the mark, check Special Standards section below for any extra matrix requirements.

3.1.6 Special Standards

The standards must be treated exactly as the samples. If the samples are extracted by first wetting the filter with ethanol (EtOH) as is routine for teflon filters, the corresponding amount of ethanol must be added to the standards. For example, if 200 □l EtOH is added to a 10 ml extraction volume, then 2.000 ml EtOH must be added to each 100.00 ml of the calibration or audit standards. If 200 □l EtOH is added to 10 ml extraction volume, add 2.0 ml EtOH to each calibration standard.

NOTE: Calcium must be analyzed in an acid matrix when the air/acetylene flame is used. The samples to be analyzed for calcium must be acidified to 0.016N HNO_3 to match the standards.

Audit standards prepared in DDW must also be adjusted to match the samples and standards. These matrix modifications are carried out in the AAS autosampler tube just prior to analysis.

For analysis of Na^+ or K^+ only, this requires the addition of 0.100 ml 1% Cs Stock Solution to each ml of audit standard, NBS rainwater or other reference standard. Since this solution is added to 1.00 ml, making a total volume of 1.10 ml, a dilution factor of 1.1 must be included in subsequent calculations. This dilution factor will apply to samples treated in this manner, also.

For analysis for Ca^{++} or Mg^{++} only, 0.100 ml of 1% La Stock Solution plus 0.010 ml 1.6N HNO3 are added to each 1.00 ml audit standard, NBS rainwater or other reference standard. This makes the dilution factor 1.11 for these two modifiers: La Stock Solution and HNO_3.

For the analysis of all 4 elements, 0.100 ml of the combined 1% La/Cs stock solution plus the 0.010 ml 1.6 N HNO3 must be added to each 1.00 ml audit standard, NBS rainwater or other reference standard. The corresponding dilution factor is 1.11.

Notice that if the audit standard must be diluted for analysis (as the case for the ERA Ca standard), the matrix modifiers can be added to the dilution flask as for the preparation of the calibration standards.

3.1.7 Preparation of NBS rainwater audit standard for use:

SRM 2694I contains Na^+, $K^+$and Mg^+ in certified concentrations (See Table 3-1). When this SRM is used as a quality control check, it must be adjusted to contain the same additives as the samples and calibration standards.

For analysis of Na^+ and K^+ only, add 0.100 ml (using the 100 µ1 Eppendorf pipet) 1% Cs stock for each 1.00 ml of rain water to the AAS autosampler tube, then add the corresponding amount of the SRM 2694I (1.000 ml for each element, using the 1000 µ1 Eppendorf pipet).

For analysis of Na^{++}, K^+, and Mg^{++}, add 0.100 ml 1% Cs/La combined stock (using the 100 µ1 Eppendorf pipet for 0.100 ml, or the 200 µ1 Eppendorf pipet for 0.200 ml or 0.400 ml) plus 0.010 ml 1.6 N HNO_3 (using the 50 □l syringe) for each 1.00 ml of rainwater to the AAS autosampler tube, then add the corresponding amount of SRM 2694I (1.000 ml for each element, using the 1000 □l Eppendorf pipet).

Prepare the AA BLANK at the same time. This blank reflects the concentration of the audit standard in matrix components, but DDW is used instead of the NBS simulated rainwater. Prepare exactly as the rainwater was prepared, using DDW.

3.1.8 Preparation of ERA Ca audit standard

The ERA Ca stock solution is 100.00 □g/ml in Ca. Because this needs dilution to 1.000 □g/ml, the modifiers can be added at the time of dilution.

Using a 10.00 ml Class A volumetric pipet prepared by rinsing with the solution to be pipetted, pipet 10.00 ml 1% combined Cs/La stock solution into a 100.00 ml poly propylene volumetric flask. Using a 1000 □l Eppendorf pipet, add 1.00 ml 1.6 N HNO_3 to the same 100.00 ml flask. Using the 1000 □l Eppendorf pipet and the balance to confirm a 1.000 g weight, pipet 1.00 ml ERA Ca stock solution into the same flask. Fill to the 100.00 ml mark with DDW and mix by inverting and swirling at least 10 times.

Prepare a Ca audit blank at the same time, using another 100.00 ml polymethylpentene volumetric flask, adding 10.00 ml 1% combined Cs/La stock solution and 1.00 ml 1.6 N HNO_3 and filling to volume with DDW.

3.1.9 Preparation of ERA Quality Control Standard

The ERA quality control standards used for AAS analysis are the Minerals WastewatR (for Na and K) and Hardness WastewatR (for Ca and Mg). The Minerals WastewatR stock solution is diluted 2:500 (or accordingly) to get the components in range for analysis . The Hardness WastewatR stock solution is diluted 1:100. Certification sheets accompany each lot and are to be

Table 3-1

Quality Control Standards

(I) NIST Simulated Rainwater Standards

	Concentrations in mg/ml	
Species	NBS 2694-1	NBS 2694-11
Fluoride	0.054 ± 0.002	0.098 ± 0.007
Chloride*	0.24	1.0
Nitrate	---	7.06 ± 0.15
Sulfate	2.75 ± 0.05	10.9 ± 0.2
Sodium	0.205 ± 0.009	0.419 ± 0.015
Potassium	0.052 ± 0.007	0.106 ± 0.008
Ammonium*	---	1.0
Calcium	0.014 ± 0.003	0.049 ± 0.011
Magnesium	0.024 ± 0.002	0.051 ± 0.003

I. WasteWatR Quality Control Standards

Parameter	Lot No. 9927 ERA Certified Value mg/l	Advisory Range mg/l
Potassium	230	207 - 253
Sodium	230	207 - 253

III. Hardness WasteWatR

Parameter	Lot No. 9927 ERA Certified Value mg/l	Advisory Range mg/l
Calcium	68	54 - 82
Magnesium	35	28 - 42

*Values are not certified

used to calculate appropriate dilutions from stock solution to working standard, and should be kept in a readily accessible folder for quick reference.

3.2 Use (What is compared with standards)

Standard Reference Material (SRM) 2694, simulated rain water, from the National Bureau of Standards is used as a cross audit check. SRM 2694 has been developed to aid in the analysis of acidic rainwater by providing homogeneous materials as control standards at each of two levels of acidity. The standard was prepared by the dissolution of high-purity salts and acids in high-purity distilled-deionized water. Certified values for SRM 2694-I and 2694-II are listed in Table 3-1. The laboratory analyst should verify the SRM for each element daily for every 50 samples as external quality control checks.

Presently, ERA quality control standards are used. The working standards as well as selected calibration standards should be prepared and analyzed by the laboratory manager or an external quality assurance auditor quarterly as an independent check. All unused working standards should be kept in the laboratory as a backup tracer until data has been properly examined and reported.

3.3 The Accuracy of Calibration Standards

The accuracy of calibration standards is primarily limited by the uncertainties or variability of the standard solution preparation and is typically within 10% of the related standard concentrations.

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram of routine atomic absorption spectrophotometry analysis is illustrated in Figure 4-1. It starts with the selection of standard operating conditions and analysis parameter set up. The samples and replicates are analyzed after the standard calibration.

4.2 Sample preparation

Make sure samples, standards and reference materials are all at room temperature. Cold samples seem to produce low signals, probably because less sample is being delivered to the flame since some of the nebulizing energy is absorbed in warming the sample.

Set up a test tube rack of AAS sample tubes labeled to correspond to the sample ID's, in the order to be analyzed as specified on the run list (see Figure 2-4, and Section 4.3). Pipet into the tubes any necessary additives (modifiers) in the amounts indicated above in section 3.1. Note the required dilution factors from the use of the

additives on the run list. Then, pipet the required amount of sample for the analysis, checking both the sample test tube and the AAS sample tube for ID. One ml is needed for each element to be analyzed, with generally 0.100 ml 1% Cs and/or 0.100ml 1% La Stock Solution per ml sample.

Figure 4-1. DRI AA analysis flow diagram.

4.2.1 Preparation of samples for analysis for Na^{++} and K^{+}

Samples will have been extracted as indicated on the analysis list (Figure 2-2). If the samples were teflon filters, they will have been wetted with 200 □l ethanol before extraction. Standards may need to be modified to correspond to the samples (see Section 3.1). Generally, samples to be analyzed only for Na and K are extracted in DDW. Because the sample extracts are used for additional analyses, the matrix modifiers cannot be added to the samples except in the AAS auto sampler tubes.

Pipet 0.100 ml (using a 0.100 ml Eppendorf pipet for 0.100 ml and the 0.200 ml Eppendorf pipet for 0.200 ml) 1% Cs stock solution for each ml of sample to be analyzed into the autosampler tube. Then pipet (using the 1.00 ml Eppendorf pipet for 1 ml sample and repeat for 2.00 ml) the corresponding sample in the correct amount into the same autosampler tube. Use 1.00 ml sample for 1 element and 2.00 ml sample for 2 elements. The pipetting of the sample from the extraction tube into the autosampler tube is done by pouring roughly the correct amount of sample into a 10 ml disposable beaker and pipetting from the beaker. This procedure maintains the sample integrity. Necessary sample dilutions can be carried out directly in the AAS sample tube if the dilution will not exceed the capacity of the tube. Matrix modifiers are added in the amount of 0.100 ml per 1.00 ml sample analyzed (or, final volume of the sample in the AAS autosampler tube). Note any dilutions on the run list and maintain the correct ratio of matrix modifiers to sample.

4.2.2 Preparation of samples for analysis for Ca^{++}

The samples will be pipetted into the autosampler tubes as for the Na and K analysis, but the modifiers are different.

If the samples were extracted in water only, pipet 0.100 ml 1% La stock solution and 0.010 ml (using the Hamilton 50 □l syringe) 1.6 N HNO_3 per 1.00 ml sample into the labeled autosampler tube. Then,pipet the sample into the autosampler tube using the procedure described in section 4.2.1.

4.2.3 Preparation of samples for analysis for Mg^{++}

Occasionally, requests are made for Mg analysis only. If the samples have been extracted in DDW, the sample matrix must be modified to correspond to the standards as used in the calibration of the AAS. Although nitric acid matrix is not necessary for the Mg analysis, generally the standards are made up in nitric acid, so the samples must be modified. The La interference suppressant must be added.

Pipet into the labeled autosampler tube 0.100 ml (using the 0.100 ml Eppendorf pipet for 0.100 ml or the 0.200 ml Eppendorf pipet for 0.200 ml) 1% La stock solution and 0.010 ml (using the Hamilton 50 □l syringe) 1.6 N HNO_3 per 1.00 ml sample. Add the nitric acid only if the samples were extracted in water. Pipet the corresponding sample and sample amount using Eppendorf pipets as described abovein Section 4.2.1.

4.3 Instrument start-up

Start with all instrument parameter knobs on right front panel at farthest point counterclockwise:

Signal---------Lamp
Mode-----------Cont
Recorder-------Abs
Gain at farthest counterclockwise position
Lamp at farthest counterclockwise position
BG Corrector---AA.

Install lamp for element to be analyzed by removing lamp and loosening the holder screws in the lamp chamber. Remove the holder with the lamp. Replace with the correct lamp in its holder. Each lamp has its own holder, so a lamp should need to be removed from a holder only when the lamp needs to be replaced. This procedure minimizes time spent aligning the lamp since it remains aligned in the holder. The alignment needs to be checked when a lamp in its holder is placed in the lamp chamber since it may have been moved.

Turn power to instrument on by pushing POWER switch on the far lower right corner of the instrument. See Table 4-1 for Standard Operating Conditions.

Turn lamp to proper current as specified on lamp for continuous operation, and as indicated in LAMP/ENERGY window on right front panel of instrument by rotating the LAMP knob in a clockwise direction, watching the indicator LAMP/ENERGY window. For Na/K lamp, current should be 12 ma; for Ca/Mg lamp, current should be 15 ma.

Select proper wavelength using the COARSE ADJUST knob and slit width for the element of interest (refer to the standard operating conditions as provided by Perkin-Elmer for the element of interest), as listed on the instrument left front panel The slit width is selected from the SLIT, nm, NORMAL side of the dial.

Set the SIGNAL control on the right hand control panel to SET UP.

Set the GAIN so a value of roughly 50 as shown in the LAMP/ENERGY window by rotating the GAIN knob gently in a clockwise direction.

Maximize the signal from the lamp by adjusting the FINE ADJUST knob to get a maximum lamp energy reading as indicated on the LAMP/ENERGY window on the right control panel. Align the lamp in the holder by adjusting the two large alignment screws on the holder and watching the LAMP/ENERGY reading. (This needs to be done only when the lamp has been changed. The adjustment should be minimal, so turn the knobs only slightly). Readjust the GAIN to get an energy reading of approximately 75.

Set the SIGNAL control to ABS by turning the knob clockwise to the ABS position.

Position the burner head only if it has been removed for cleaning and replaced. With the burner head clearly not interfering with the path of the light from the lamp to the signal receiver, press AZ to zero the

Table 4-1

Standard Conditions for Atomic Absorption

Chemical Species	Wavelength (nm)	Slit Width (nm)	Flame Gases
Na^{+}	589.0	0.7	Air-Acetylene
Mg^{++}	285.2	0.7	Air-Acetylene
K^{+}	766.5	2.0	Air-Acetylene
Ca^{++}	422.7	0.7	Air-Acetylene

reading. (The location of the burner head can be seen by placing a piece of paper between the burner head and the left hand wall of the burner compartment and observing the lamp image). Find the maximum height of the burner head by rotating the BURNER HEAD VERTICAL ADJUST KNOB (marked with a V) so the head rises until a reading greater than zero is seen. Subsequent burner head adjustments must not raise the burner head above this level.

Check the level of liquid in the drain jug, empty if too high, fill up to the line drawn on the jug. Check the acetylene level (replace tank if pressure falls below 520 kPa). Turn on exhaust fan. Turn on AIR valve (left front panel of instrument), check that flow rate is 40. Adjust with OXIDANT FLOW knob, if necessary. Turn on FUEL using toggle switch to point straight out, check that flow rate is 20. Adjust with FUEL FLOW knob, if necessary. Ignite flame with lighter by holding the lighter flame near the opening of the burner head. Lower probe into water beaker by pressing MANUAL on the AUTOSAMPLER CONTROLLER. Always turn on air first, then fuel and light. When flame is lit, aspirate water or sample. To warm up instrument, let water aspirate through flame for about 15-30 minutes.

Adjust the location of the burner head only after it has been removed for cleaning and replaced. To adjust burner head location, aspirate the standard which produces an absorbance of about 0.200 absorbance units while moving the burner head horizontally by turning the left hand knob marked H and watching the READOUT window until maximum absorbance is observed; then, rotate the burner head to achieve maximum absorbance using the knob located back in the burner chamber to the right of the burner head assembly; then, lower the burner head from its maximum position by turning the right knob at the bottom of the burner head assembly marked V to check if absorbance increases. The sensitivity of the signal to burner head location for one element compared to another for the four elements presently analyzed using these procedures is small, so these adjustments do not have to be made when changing from analysis for one element to another.

Adjust nebulizer only after it has been removed and taken apart for cleaning. This cleaning is done only if necessary, probably about once per year. To adjust nebulizer to maximize absorbance, aspirate the standard which produces an absorbance of 0.200 and rotate the front nut of the nebulizer until bubbles come into the tube. Then tighten the knob again until a maximum absorbance is observed. The Environmental Analysis Facility, EEEC center, currently uses a high performance Platinum/Iridium nebulizer with the Perkin-Elmer 2380 AAS. NEVER ADJUST THIS NEBULIZER ON A NITROUS OXIDE/ACETYLENE FLAME. To achieve the higher sensitivities characteristic of the high performance nebulizer, gas flow rates must be set lower than recommended in the PE methods manual or the Standard Conditions manual (approx. 80% of recommended values). Consult the PE High Performance Nebulizer Publication #B3112 for installation, adjustment, and maintenance instructions.

On the right control panel, set MODE to HOLD. Set integration TIME to 0.4 by pressing "0.4", "t" (this sets integration time at 0.4 seconds). Average 8 readings by

pressing "8", "AVE". Set Standard Deviation (SD) and PRINT on by pressing these buttons.

4.3.1 Data Collection

Select AA computer settings to accumulate data:

Turn computer on by flipping the power switch located at the back left side of the computer, insert a disc to collect absorbance readings.

At the C:\ prompt, type “copy compr prn”

Select the proper directory by typing
"DIR/p" return
This lists the directories one page at a time. Select any key to get the next page.

Switch to the proper directory by typing
"CD\xxxxx" return
This selects the main directory, where xxxxx is the name of that directory.

Select a proper subdirectory (if necessary, usually AA) by typing
"CD\xxxxx\AA" return

Call up data accumulation program by typing
"AACOM" at the DOS prompt (C:\>), return.
The AACOM program accumulates data in the computer and prints the absorbencies as they are read by the AA.

- Run list (See section 2.3)

The run list (see Figure 2-4) must be maintained on a written sheet since there is no way to enter a sample ID into the data collection program at this time. The run list is prepared before the run is started and samples and standards are run in the order indicated. Standards in increasing order from blank to 1.500 □g/ml, QA standard (usually ERA Mineral or Hardness WastewatR) (), AA BLANK, other QA standards and blanks.

Samples, replicates and standards in this order:

10	Samples
1	Blank
1	Replicate
1	Blank
1	Standard (approximating expected value, or range)

1 Blank

Repeat this sequence as necessary to complete all sample analysis.

This sampling order maintains the recommendation of one replicate every 10 samples, and one standard every 10 samples. A blank is run every 10 samples to minimize any sample carryover concerns. If any dilutions are made, a dilution blank should be analyzed as one of the samples. An AA BLANK consisting of any modifiers and a volume of DDW corresponding to the volume of sample should also be prepared and run as a sample. This last is to check any possible deviation of the AA standard blank with the actual preparation of the samples.

Any additional dilutions must be entered on the run list as the samples are prepared. The computer run number must be entered on the list as the samples are run, but absorbencies do not need to be recorded as this can be recovered from the printed copy of the collected data.

Label the run list with the name of the raw data file, its corresponding database file, the date, the element and the analyst's initials.

Generally, the sample tray is filled with samples and QA standards, so the calibration is done by aspirating the calibration standards manually. Aspirate the blank by lifting the probe from the DDW beaker by pressing MANUAL on the autosampler control box. Press AUTO ZERO. This will be entered as #l on the data in the computer. Read standards and samples in ABSORBANCE, use the computer to convert the data into concentration during data entry. Read the blank by pressing READ. This will be #2 in the data file. Read the standards in increasing order by removing the tube from the probe, aspirating another, and pressing the READ button. After the AVERAGE is printed out, the sample can be removed from the probe. Refer to previous runs to check if standards are yielding a similar absorbance. Even if the standards yield different absorbencies than previously, if a plot of absorbance vs. concentration gives a smooth curve (not linear at higher concentrations), the readings may be used. Read the absorbance of the ERA standard prepared with any necessary modifiers as outlined in 3.1.6., and its corresponding blank (AA blank). It is usually at this point that any method blanks are run to check for gross contamination during extraction of the samples.

When absorbancies for the calibration curve and the QA standards have been collected, copy them onto the runlist and enter

absorbancies and concentrations into the AACAL program on the desk computer (see section 5.1 for operation of AACALculation program).

If the calibration curve and audit standard are acceptable, proceed with analysis using autosampler.

4.4 Routine operation with Autosampler

Samples can be introduced into the AAS manually by holding a sample tube up to the probe, or using the autosampler. The autosampler can calibrate using 3 standards if the AAS is in the CONCENTRATION MODE. In the ABSORBANCE MODE, it seems easiest to auto zero and read standards manually so there is maximum space in the autosampler for samples. Note that when the AAS is not being used for analysis (as in warm-up or while loading trays), the probe should be in the rinse beaker so water is being aspirated at all times. The auto sampler is returned to this rest position by pressing RESET, then MANUAL to lower the probe into the beaker. This position is used when samples are introduced manually, as at the beginning when the standards are read.

4.4.1 Autosampler settings

Since measurements are made in the ABSORBANCE MODE, the number of standards (# STD) is zero. In routine analysis, the AZ, Sl, S2 and S3 spaces at the beginning of the analysis are not used. The autosampler is advanced to position 1 by pressing "1, MANUAL", then the START/STOP button is pressed for routine analysis. (If the autosampler is not advanced to position 1, in the absorbance mode, the Auto Zero will be reset (AZ). In general, this is undesirable since the standards were read before the auto sampler was set in use. If the standards are included as the first several samples, this option could be used.)

Set READ DELAY to 3 (3 seconds), READ TIME to 5 (5 seconds). This read delay allows time for the preceding sample to be washed through before readings are taken on the current sample. The read time is long enough to let all 8 readings to be taken. This sampling time requires about one ml of sample.

Load the auto sampler tray from the run list, enter the number of the last sample by typing "number of last sample", LAST SAMPLE.

4.4.2 Sampling Sequence

The order of samples and standards in the autosampler carousel is as in the run list, as follows:

Positions 1-10 : Samples

Position 11 : Blank

Position 12 : Replicate

Position 13 : Blank (as used in Auto Zero)

Positions 14 : Standard (approximating expected value, or range)

Position 15 : Blank

Position 16-25 : Samples

(Page 2 of analysis list)

Positions 26 : Blank

Position 27 : Replicate

Position 28 : Blank

Position 29 : Standard

Positions 30 : Blank

Position 31-40 : Samples

Position 41 : Blank

Position 42 : Replicate

Position 43 : Blank

Position 44 : Standard

Position 45 : Blank

Position 46-50 : Samples

This sampling order maintains the recommendation of one blank every 10 samples, one replicate every 10 samples, one standard every 10 samples. If there are more samples to be analyzed than will fit into one tray, the first part of the tray may be unloaded and filled with new samples, replicates, blanks, and standards, while the last part of the tray is being analyzed. Any necessary dilutions can be made and added at this point. Make certain that any overrange replicates are diluted and rerun, also. If any dilutions are made, a dilution blank should be analyzed as one of the samples. An AA blank

consisting of any modifiers and a volume of DDW corresponding to the volume of sample should also be prepared and run as a sample. This last is to check any possible deviation of the AA standard blank with the actual preparation of the samples.

4.4.3 When data collection is complete, press "ESC" to get out of the data accumulation program. The program then prompts for the name of a file to save the data. The data are saved to the C: drive at the end of data collection by typing "projdate.element" (where "projdate"= 2 letter symbol for the project name, four digit month and date) and the "element" extension is a two letter symbol for the element and the number of the analysis run (example: SB0516.Nal = Santa Barbara samples run 05/16, sodium 1) when requested.

These data are transferred to a floppy disk to be used in calculating the concentrations from this absorbance data using dBase.

Type "copy 'projdate.ele' a:" to copy the file to a floppydisc.

4.4.4 If another element on the same lamp is to be analyzed, the sample tubes must have been loaded with the appropriate amount of sample (l ml per element). It is necessary to merely change the wavelength, recall the data collection program on the computer (AACOM), read the standards for the second element and proceed with the analysis on the autosampler (see Section 4.3.1).

While the analysis on the AAS is taking place, the next rack of samples can be prepared.

4.5 Shut-Down

After all analyses are complete and checked for reproducibility and accuracy (QA standards), water is aspirated through the burner chamber to clean the chamber by pressing the MANUAL button on the autosampler to lower the probe into the rinse beaker. After 5 minutes, the probe is lifted from the rinse beaker by again pressing the MANUAL button on the autosampler.

The flame is turned off from the left hand control panel of the instrument by flipping the FUEL toggle to the down position. After the flame goes out, the air is turned off by turning the oxidant valve to the OFF position. MAKE CERTAIN THIS ORDER IS FOLLOWED - FUEL SHUT OFF FIRST, THEN AIR SHUT DOWN. TURNING THE AIR OFF FIRST WILL CAUSE AN EXTREME FIRE HAZARD. The exhaust fan can now be turned off.

The instrument is turned off from the right hand control panel by turning the SIGNAL knob to the SET UP position and rotating the GAIN knob to its furthest counterclockwise position. Next, the SIGNAL knob is turned to the LAMP position, and the LAMP knob is rotated to its furthest counterclockwise position. The MODE

knob is returned to the CONTINUOUS setting. The POWER switch is now turned to the OFF position.

The computer is turned off by flipping the POWER switch.

The printer is turned off by flipping the POWER switch.

The autosampler is left on.

5.0 QUANTIFICATION

5.1 Calculations

5.1.1 Since the measurements are taken in Absorbance, the readings must be converted to concentrations based on the standards. This is presently performed using the AACALculation program.

The absorbencies are entered into a data base as follows:

From the MS-DOS prompt (C:\>) select the proper directory.

To get a listing of directories, one page at a time, type "dir/p" (return).

To view additional pages, press any key.

Change to the proper directory (selected from the listing according to the project) by typing "cd\xxxxxx" (return) where xxxxx is the name of the directory.

Often a subdirectory is used to store AAS data, so obtain a listing of the sub directories of the selected directory by typing
"dir/p" (return)
AAS data are stored in the subdirectory called "AA"

Change to the AA subdirectory by typing
"cd\xxxxx\aa" (return)
(This can be done at the first step if an AA directory does not need to be made)

If an AA subdirectory does not already exist, create one by typing
"md aa" (return)

Once the correct directory and subdirectory have been entered, the AACAL program may be brought up. THE OPERATOR MUST FIRST LOG INTO THE P: DRIVE (PROGRAM DRIVE) OF EAFMAIN ON THE NETWORK.

Type AACAL, then <enter> twice. A blank absorbance/concentration table will appear on the screen. Enter absorbance and concentration values of the calibration standards from the run list (0-1.5 µg/ml), using arrow keys to move around the screen.

Press <F2> (Relationship) key. A cursor square will appear below the Fn1 (Function 1) column. To establish a linear regression for calibration points, type <L> until maximum curve linearity is obtained. Function 1 data will appear on the right side of the screen (no. of data points used, correlation, slope, and y-intercept). MINIMUM ACCEPTABLE CORRELATION IS 0.9900. A correlation of greater than 0.99 is normally obtained on Na, K, Mg, and Ca by functioning the curve in 3 segments: 0-0.500 µg/ml (Fn1), 0.500-1.000 µg/ml (Fn2) , and 1.000-1.500 µg/ml (Fn3). There will now be 3 sets of function data on the right side of the screen, one for each segment of the calibration curve.

There is room for 5 sets of function data in the AACAL program. Absorbance and concentration data points from different sections of the curve can be entered, and from the resulting function data a determination of the most accurate function to use can be made. To move around in the function field, the cursor arrows may be used.

To obtain a screen view of the resulting calibration curve, press <F3>. Each function of the curve will be shown as a different color corresponding to the colors of the Fn column.

At this point, the QA standards used for the forthcoming analytical run can be calculated:

Press <F5> (Calculate), then <1> (Manual). Enter absorbance value and dilution factor.

The AACAL program will calculate concentration in µg/ml for the data points entered, and will show which function (segment of the curve) was used to obtain that concentration. Enter <Y> and sample ID to send this information to the printer. If more than one function has been used to calculate the concentration value, the program will ask the operator to select which function comes closest to the actual value of the standard used. Enter function to be used by its number (1,2,3,4,or 5). If the QA value is acceptable (± 10% of given value), proceed with the analytical run by starting the autosampler.

AACAL can be used to calculate replicate and standard check values during the analytical run by returning to the <F5> key and entering absorbance value and dilution factor in the same manner as the QA standards.

To obtain a hard copy of the calibration curve, function data, and any calculated QA or replicate values, press <F4> key, enter project description, species analyzed, raw (absorbance) data file name, and dBase file name. Press <Y> to print.

When analytical run has been completed and absorbance data file copied onto a floppy disk (Section 4.4.3), load floppy disk into desk computer.

Press <F5>, then <2> (ASCII file→dBase file). If a hard copy for this file has previously been obtained, species and file information will have already been entered. If not, enter this information now. The screen will show dBase conversion taking place, then "dBase conversion completed." If another file is to be entered, return to beginning of AACAL program by pressing <F6> (Initialization). To exit from AACAL program and return to DOS, press <esc>.

Once the correct directory is being used, go into dbase by typing "dbase" <enter>. At the dot prompt, type " use filename" <enter>. The AACAL program dBase conversion will have automatically entered absorbances, analysis date, slope and intercept fields,and will have calculated sample and standard calculations in µg/ml.

Type "brow". In the BROWSE mode, enter the sample ID's (QID) from the run list checking the computer run number with the file number and the absorbance from the hard copy of the original data.

Enter standard, blank, replicate and quality assurance flags into flag field (naaf, kpaf, mgaf, caaf) as follows:

q1	standard check
q4	standard used in calibration
r1	replicate samples (further replicates, use r2, etc.)
b1	field/dynamic blank
b2	laboratory control blank
b3	distilled water blank
b4	method blank
q2 or q3	extract/solution blank, AAblank
q2	QA standard other than NBS (ie, ERA stds)
q3	NBS QA standard
q5	spike tests
v	void

Next, area factors (AREAF), extraction volumes (EXTVOL), dilution factors (NAADILF, KPADILF, CAADILF or MGADILF) are entered as follows:
Type:

"replace all extvol with nn" (return)

where nn is the extraction volume in milliliters

"replace all areaf with aa" (return)

where aa is the inverse of the fraction of filter used in the extraction

"replace all naadilf with dd" (return)

where dd is the dilution factor applied to the majority ofthe analyses in the set, as described on the run list notes.

After the flags have been entered, any changes in extraction volume, area factors and dilution factors can be made by reference to the flags, for example

"replace extvol with 1 for naaf='ql'.or.naaf='q2' .or.naaf='q4'"(return)

For example, the standards will have a dilution factor of 1, while the samples, QA standards, and NBS rainwater will have dilution factors dependent on the additives or subsequent dilutions. Extraction volumes and area factors for standards and rainwater are 1.

To check accuracy of data entry ,type :

"brow fields
qid,naaf,naac,naaml,naaabs,naadilf,areaf,extvol,comment"

This will bring up the fields in which the data has been hand entered and allow a cross check to verify accuracy of these fields versus the absorbance data.

The concentration of element in µg/ml (naaml, kpaml, mgaml, caaml) has been calculated through the AACAL program. To achieve this calculation manually:

type: "replace all naaml with naaabs*naaslope+naaint" (return)

Calculate the concentration (NAAC, KPAC, MGAC or CAAC) on the filter as follows:

type: "replace all naac with naaml*naadilf*areaf*extvol" (return)

Finally, after all data is entered and all calculations made, get a hard copy of the data by typing
"run copy\compr prn" (return) to change the printer to compressed print
"list to print" (return)

Make a copy on a disk by typing
"run copy zzzzz.dbf a:" where zzzzz.dbf is the name of the database file.

5.2 Precision Estimates

The precision for samples analyzed over selected time periods is calculated by the methods described in Watson et al.(1983). For replicate analyses, the precision of the ionic species C, on each sample extract is

$$C = \left[\frac{1}{n} \sum_{i=1}^{n} \left(C_1 - C_2 \right)^2 \right]^{1/2}$$

where:

n = number of replicates
C_1 = ionic concentration derived from routine analysis
C_2 = ionic concentration derive from replicate analysis

This precision contains the uncertainty due to the inhomogeneity of the deposit across the filter surface as well the uncertainty of the ion analysis. When calculating ambient concentrations, analysis precision is combined with field blank variability and sampling volume uncertainty to estimate measurement uncertainty.

6.0 QUALITY CONTROL

The quality control procedures serves two purposes: 1) to identify the possible problems with the measurement process, and 2) to calculate the precision of the ion measurements.

6.1 Performance Testing

Besides the daily start-up described in Section 4.0, the analysis sequence for standards, blanks, and replicates should be followed as specified in Section 4.3. After every ten samples, one replicate sample will be analyzed. The replicate should be from the previous day's run. In the case of a new project starting, with no previous analysis of the samples, the replicates can be chosen from the set of 10 just run, the next replicate would also be from that first set, and the ones after that from the set preceding the current one by two.

After each group of ten, a standard, a blank, and a replicate will be run. The standard and replicate will be evaluated, and the data recorded on a QA chart, kept by the instrument for this purpose. Running a blank after every 10 samples serves 2 purposes: (1) to eliminate carryover between samples of high concentration, and (2) to indentify any problem with baseline drift or shift. Figure 6-1 is an example of the QA chart to be used. The equation for the calculation of the replicate percent error is as follows:

$$\text{Error \%} = \frac{\left(R_{1i} - R_{2i}\right) \times 100}{\left(R_{1i} + R_{2i}\right) \div 2}$$

where:

R_{1i} = concentration of sample I
R_{2i} = concentration of the replicate analysis of sample I

For calculation of the standard percent error:

$$\text{Error \%} = \frac{\left(S_i - S\right) \times 100}{S}$$

where:

S = concentration of the working standard
S_i = concentration of standard obtained from the replicate analysis

Figure 6-1. DRI AA quality control chart.

6.2 Control Charts, Tolerance and Actions to be Taken

Maintain a QC chart of the absorbencies of selected standards and the NBS rainwater to monitor the performance of the instrument. An absorbance suddenly way off would indicate a contamination. Gradual change in the absorbance would indicate the growing need to reset instrument parameters to readjust absorbance to the maximum.

The permissible range of error is a function of concentration and the element to be analyzed as stated in section 1.5 with a larger percent error range tolerated for lower concentrations. Ranges of errors depend on the species analyzed because sensitivity varies with analyte. Sodium and potassium have approximately the same sensitivity, so the expected ranges of error for these two elements are the same: ±30% for concentrations less than 0.100 □g/ml; ±20% for concentrations between 0.100 and 0.150 □g/ml; and ±10% for concentrations greater than 0.150 □g/ml. Calcium is approximately ten times less sensitive under the instrument conditions currently used, so the ranges of error would be expected to shift by that factor: ±30% for concentrations less than 1.000 □g/ml; ±20% for concentrations between 1.000 and 1.500 □g/ml; and ±10% for concentrations greater than 1.500 □g/ml. Magnesium is roughly twice as sensitive, so the range of error would shift correspondingly: ±30% for concentrations less than 0.050 □g/ml; ±20% for concentrations between 0.050 and 0.100 □g/ml; and ±10% for concentrations greater than 0.100 □g/ml.

If replicates exceed the tolerances as calculated in section 6.1, the sample will be rerun to check for a spurious result. If the replicate is still in variance, standards should be rechecked, any dilutions redone and appropriate blanks checked. After the reason for error is discovered, samples analyzed after the replicate preceding the one in variance must be reanalyzed using the corrected procedure.

6.3 Record Keeping

A manila folder, with clips, will be used to keep the analyses records together. Data in the folder will be organized in the following sequences:

- The sample run list,(the order in which the samples were analyzed, including replicates and standards.)
- The method used for the analysis.
- AACAL program printouts which include calibration curves for the analyzed species, corresponding correlation and function data, and calculations for QA standards.
- A charts for replicates.

- QA charts for Standards.

The manila folder will be dated and labelled with the project name and filed in the proper cabinet. The original analysis list request is filed in a 3 - ring binder labeled by year, and stored on a shelf to the left of the AA instrument.

6.4 Data Validation Feedback

The sample validation philosophy follows the three level approach devised by Mueller and Hidy et al. (1983) in the Sulfate Regional Experiment (SURE). Level I sample validation takes place in the field or laboratory and consists of:

- Flagging samples when significant deviations from measurement assumptions have occurred.

- Verifying computer file entries against data sheets.

- Eliminating values from measurements which are known to be invalid because of instrument malfunctions.

- Replacing date when re-analysis have been performed.

- Adjusting measurement values for quantifiable calibration of interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master data base. Level II applies consistency tests based on known physical relationships between the variables in the assembled data.

Level III sample validation is part of the data interpretation process and will be performed by each project manager and subsequent data users. The first assumption upon finding a measurement which is inconsistent with the physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. The project manager should review all the QC data as soon as it becomes available and ensure the feedback from the QC results to the routine operations. The project manager should consult with the QA officer to initiate and document changes to the data base as they are needed.

7.0 QUALITY ASSURANCE

The performance and system audits are scheduled on a biannual basis by the QA officer to ensure that all procedures are followed properly and to verify the precision, accuracy and validity of the data.

8.0 REFERENCES

ACS (1983). American Chemical Society (ACS) Committee on Environmental Quality (1983). Principles of Environmental Analysis. Analytical Chemistry 55: p. 2217.

Mueller (1983). Mueller, P. K., G.M. Hidy, J.G. Watson, R.L. Baskett, K.K. Fung, R.C. Henry, T.F. Lavery, and K.K. Waren (1983). "The Sulfate Regional Experiment: Report of Findings, Volumes 1, 2, and 3." Report EA-1901, Electric Power Research Institute, Palo Alto, CA.

Perkin Elmer (1987). #0993-9575 Instructions, Model 2380 Atomic Absorption Spectrophotometer, September, 1987. Perkin Elmer, Norwalk CT.

Perkin Elmer (1980). #047-0096, 047-0097 Model AS-50 Flame Auto Sampler for Atomic Absorption, December, 1980. Perkin Elmer, Norwalk, CT.

Perkin Elmer (1982). #0303-0152 Analytical Methods for Atomic Absorption Spectrophotometry, January, 1982. Perkin Elmer, Norwalk, CT.

Perkin Elmer (1991). #B3112 High Performance Nebulizer Technical Documentation, Bodenseewerk Perkin-Elmer GmbH